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THE
PHYSICAL REVIEW.

ON THE GAMMA-RAY ACTION OF EXTENSIVE FLAT RADIUM PREPARATIONS AT DIFFERENT DISTANCES WITH AND WITHOUT ABSORBING MATERIALS.

By Victor F. Hess.

Synopsis.

Intensity of gamma-radiation from a radium-covered disk at points along the central normal, with and without absorbing layers, is of interest in connection with the use of radium applicators for gamma-ray treatments. By integrating the effects of narrow rings of the active material, a *theoretical formula is derived* for the intensity at a distance p from a disk of radius R if the rays go through one or more filters whose absorptions are known and through a thickness of tissue h_0. This formula involves the so-called exponential integral for which tables are available. Numerical values have been calculated for certain special cases and these are given in two tables which enable the intensity to be determined at various distances from any uncovered disk in air and also from any disk covered by a layer of brass 2 mm. thick. A given amount of radium spread on a 4 cm. disk gives at distances greater than 4 cm. about the same intensity as when concentrated on the end of a small tube, but the effect near the active layer is over ten times less intense in the former case. This result shows that burns of the skin may be avoided by using sufficiently large disks without decreasing the depth action materially.

New unit of gamma-ray intensity is proposed, to be called a *milli-eve* and to be defined as the intensity at a distance of 1 cm. from a point-shaped radium preparation of one milligram.

Introduction.

THE "flat radium applicators" consist mostly of a metallic disk covered on one side with a lacquer, with which some radium salt is mixed. The shape of the disk may be rectangular or circular. The calculation is given for circular disks and may be applied for other shapes with sufficient accuracy. In order to cut off all alpha and most of the beta rays the surface of the radium disk is covered by a metallic disk. This "filter-disk" consists of brass, copper or similar materials and has a thickness of 1–2 mm. A second filter, made of a material of low atomic weight (celluloid, rubber, etc.) is applied to absorb the secondary β-rays, which come out from the metal disk. The thickness of

this second disk is relatively small (1–3 mm.). The absorption of the primary γ-rays in this layer may therefore be neglected.

THEORY OF THE GENERAL CASE.

Fig. 1 illustrates the general case. The radioactive layer (circular area of radius R) is considered as a disk of infinitely small thickness and σ represents the quantity of radium per sq. cm. The metallic filter has a thickness d_0 and is applied directly below the radioactive disk.

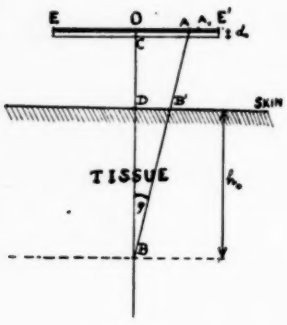


Fig. 1.

The radius of the disk is

$$R = OE, \qquad R = OE'.$$

The point at which the intensity of the γ-rays is considered is B.

We call the distances

$$OA = r, \qquad OB = p,$$
$$OC = d_0, \qquad BD = h_0.$$

The last-mentioned letter indicates the thickness of tissue, which has to be traversed before point B is reached.

Now we take an arbitrary point A on the radioactive disk and consider the action of the ring-shaped element of area of the width $AA_1 = dr$ at the point B.

The action of the γ-rays of this element at B without any absorption would be

$$dQ = K \cdot \frac{2\pi r \cdot dr \cdot \sigma}{p^2 + r^2},$$

where K indicates the so-called "Eves number"; that is the number of pairs of ions, generated by the γ-rays of 1 g. of radium at the distance 1 cm. from the source of rays.

The γ-rays coming from A traverse the metallic filter and the tissue in an oblique direction according to an angle $\varphi = \sphericalangle OAB$. We call the absorption coefficient in the metal-filter μ, in the tissue ν.

The factors which express the real absorption of γ-rays in the filter and the tissue become therefore

$$e^{-\frac{\mu d_0}{p}\sqrt{2p+r^2}} \quad \text{and} \quad e^{-\nu h_0 \sqrt{p^2+r^2}}.$$

Their product corresponds to the total absorption.

Thus we get for the real intensity of γ-rays at point B, created by the

rays of the ring-shaped element dr, the expression

$$dQ = 2\pi K\sigma \frac{rdr}{p^2 + r^2} \cdot e^{-\frac{\mu d_0 + \nu h_0}{p}\sqrt{p^2+r^2}}.$$

For simplicity we may write

$$\frac{\mu d_o + \nu h_o}{p} = b.$$

This expression represents a constant for every special distance.

To find the total amount of the γ-ray intensity at B we have to integrate dQ over the whole area of the disk. Thus we obtain the integral

$$Q = 2\pi K\sigma \int_o^R \frac{re^{-b\sqrt{p^2+r^2}}}{p^2 + r^2} dr. \qquad (1)$$

It is easy to reduce this integral to a known form by introducing the new variable $u = b \cdot \sqrt{p^2 + r^2}$.

Therefore the integral becomes

$$Q = 2\pi\sigma K \int_{b.p}^{b.\sqrt{p^2+r^2}} \frac{e^{-u}}{u} du \qquad (2)$$

The integral $\int (e^{-u}/u)du$ is commonly called "the exponential integral." Numerical values of this integral are given by J. W. L. Glaisher,[1] W. L. Miller and T. R. Rosebrugh [2] and others.

We call as usual

$$-\int_a^\infty \frac{e^{-u}}{u} du = Ei(-a).$$

The corresponding value of this integral may be taken directly from the tables for all values of a. A transformation of formula (2) leads to the expression

$$Q = -2\pi\sigma K[Ei(-b \cdot p) - Ei(-b \cdot p\sqrt{p^2 + R^2})].$$

After substituting for b we obtain the general solution

$$\dot{Q} = 2\pi\sigma K\left[Ei\left(-\frac{\mu d_0 + \nu h_0}{p}\sqrt{p^2 + R^2}\right) - Ei(-\mu d_0 - \nu h_0)\right]. \qquad (3)$$

By introduction of the numerical values we obtain thus directly the ionization created by the γ-rays at the chosen distance from the disk after allowing for the absorption in the filter and the tissue. When the values of Q for different distances p are calculated the law of decrease of intensity of the gamma-radiation in each special case may be obtained.

[1] J. W. Glaisher, Phil. Trans., Vol. 160, p. 367 (1870).

[2] W. L. Miller and T. R. Rosebrugh, Trans. Roy. Soc. of Canada, 3 Series, Vol. 9, sect. 3, p. 73 (1903).

Formula (3) may be easily applied also in cases, where several different filters are used. In these cases we have simply instead of μd_0 to introduce the sum $(\mu d_0 + \mu' d_0' + \cdots)$ where μ and d_0 denote the absorption coefficients and respective thicknesses of the different filters used.

It can also be seen from formula (3) that Q is independent of the unit of length used for p and R; that it depends only on the ratio $\frac{p}{\sqrt{p^2 + r^2}}$, which is the cosine of the angle subtended by the radius of the disk. Therefore the effect at 4 cm. from a disk of 2 cm. diameter is the same as at a distance of 2 cm. from a disk of 1 cm. diameter. This holds of course only when σ, the quantity of radium per unit of area, is kept constant. In the numerical tables which are given later not σ but the total radium content of disks of different diameters is taken as constant. This corresponds more to the actual conditions of medical use.

Different absorbent materials have the same effect, when the products of absorption coefficient and thickness of layer have the same numerical value. Thus a layer of brass (thickness d_0) and a layer of tissue (h_0) are equivalent, when $\mu \cdot d_0 = \nu \cdot h_0$.

SPECIAL CASES.

1. Action of the γ-rays of a radium disk, covered by a metal screen (thickness d_0) in air.

This case is of interest, for it gives the actual amounts of ionization. by the γ-rays of the disk, when no tissue is between the source and the chosen point (for instance a point directly on the surface of the skin). This case corresponds to $h_0 = 0$ and formula (3) changes into the simpler form

$$Q = 2\pi\sigma K\left[Ei\left(-\frac{\mu d_0}{p}\sqrt{p^2 + r^2}\right) - Ei(-\mu d_0)\right]. \qquad (3')$$

2. Action of the radium disk without any absorbing filters: This case is physically not without interest: from this it is possible to judge upon the difference in the distance-action of a disk and an approximately point-shaped source of radiation. For $d_0 = h_0 = 0$ formula (3) becomes indefinite. Thus we have to go back to formula (1). Here the exponential factor becomes 1 and the integral leads to the simple solution

$$Q = 2\pi\sigma K\left[1{\cdot}1513 \cdot \log_{10} \cdot \frac{p^2 + R^2}{p^2}\right] \qquad (1')$$

(for greater convenience in practical cases Briggs's logarithms are introduced).

Practical Applications and Proposal of a New Unit for the Intensities of Action of the γ-Rays.

In the numerical computations of the formulas (1)–(3) given above it will be found troublesome to express Q in terms of K (number of pairs of ions, created per c.c. and sec.), because K is a very high number (*Eve* found, that in air $K = 3 \cdot 9.10^9$ ions/ccm. sec.). In most cases relative numbers, for instance the expressions within the brackets, would suffice.

However, for a greater convenience of use, expecially for physicians, a new unit for γ-ray intensities may be proposed: The action (ionization) of the γ-rays of RaC in equilibrium with 1 gram of radium, given as a nearly point shaped source (very small tube) at the distance of 1 cm. from this source may be called "*1 Eve.*" The one thousandth part of this intensity be called "*1 Milli-Eve.*" According to this definition[1] a small radium-tube of 50 mg. radium element would give (by its γ-radiation) in the distance 1 cm. 50 Milli-Eves; in 2 cm. (corresponding to the inverse square of distance-law, 12.5 Milli-Eves; in 3 cm. 5.56 Milli-Eves; in 0.5 cm. 200 Milli-Eves, etc.

According to that the total amount of γ-radiation used in one exposure may be expressed in Milli-Eve hours, that is the product of the number of Milli-Eves into the number of hours of exposure.

To express the results of the formulas of this paper in Milli-Eves, we have to consider that according to the definition of this new unit the intensity of a point-shaped and unfiltered radium preparation at 1 cm. distance has to be taken as 100 when a source of 100 mg. is used. When we use a filtration of 2 mm. brass, the intensity at the same distance would be about 90 and all other intensities have to be changed in the same proportion.

In the following tables it is assumed that 100 mg. preparations are used. For other amounts the figures have to be altered accordingly.

The values of the exponential integral $Ei(-a)$ are taken from abbreviated tables, given in Meyer and Schweidler's "Radioactivity" (Teubner, Leipzig, 1916). The coefficient of absorption of the complex γ-radiation of RaB and RaC has been assumed as $\nu = 0.094$ cm. This is an average of experimental values found by G. Failla (Amer. Journ. of Roentgen., Vol. 3, 215–232, 1920) and A. Fernau (Strahlentherapie, Vol. 9, p. 236–254, 1918).

Table I. shows the γ-ray-intensities at different distances from a circular disk (4 cm. diameter), covered uniformly with 100 mg. radium for three cases: without any filter (formula 1′), with a filter of 2 mm.

[1] Prof. A. S. Eve (Montreal, Canada) was the first who determined the absolute values of the ionization of γ-rays at different distances from a known radium source. A. S. Eve. Phil. Mag. (6), 12, 189 (1906); 22, 551 (1911); 27, 39 (1917).

brass (formula 3′) in air and in tissue. Column 3 gives the figures in the case, when the same filtered disk is directly applied above the skin. All figures in this column are considerably lower than in column 2 according to the absorption in the tissue.

TABLE I.

Radium Disk, 4 cm. diameter, 100 mg. Radium.

Distance from the Surface of the Radium Disk (Cm.).	γ-ray Intensities in Milli-Eves.		
	No. 1, Uncovered Disk in Air.	No. 2, Disk Filtered by 2 Mm. Brass in Air.	No. 3, Disk Filtered by 2 Mm. Brass in Tissue.
$p =$ 0.3	107.4	81.2	79.7
0.5	80.0	64.9	61.5
1.0	45.4	38.9	35.4
2.0	19.5	18.1	14.9
3.0	10.3	8.5	6.8
4.0	6.3	5.1	4.2
5.0	4.2	3.4	2.7
6.0	3.0	2.3	1.6
7.0	2.1	1.8	1.1
8.0	1.7	1.4	0.8
10.0	1.1	0.8	0.5

As a second example the intensities of the γ-radiation have been calculated for circular disks of the same radium amount but different diameters, varying from 0.4 to 8.0 cm. The smallest type of these disks corresponds to a practically point-shaped radium-source (very small tube). The figures in the following Table II. are again given in Milli-Eves.

TABLE II.

Distance from the Surface of the Radium Disk in Cm.	γ-ray Intensities (in Milli-Eves) (all Disks Filtered by 2 Mm. Brass).				
	Disk of 0.4 Cm. Diameter.	Disk of 1.0 Cm. Diameter.	Disk of 2.0 Cm. Diameter.	Disk of 4.0 Cm. Diameter.	Disk of 8.0 Cm. Diameter.
$p =$ 0.3	888	528	215	81	24
0.5	341	289	154	65	21
1.0	90	82	72	39	16
2.0	22	22	21	18	9.7
3.0	10	10	9.5	8.5	6.4
4.0	5.6	5.7	5.5	5.1	4.5
5.0	3.6	3.6	3.6	3.4	3.1
6.0	2.5	2.4	2.4	2.3	2.2
7.0	1.8	1.9	1.8	1.8	1.7
8.0	1.4	1.4	1.4	1.4	1.3
10.0	0.8	0.8	0.8	0.8	0.8

It is easily to be seen from this table that the intensities of the γ-rays of the smallest and the largest disk on the surface vary in the proportion 888 : 24; the action in the depth (from 3 cm. on) is nearly the same with all the disks. The use of large radium disks is therefore recommendable in all cases, where the action of points near the preparation itself should be as small as possible (for instance to avoid burns of the skin).

Physical Research Laboratory,
The United States Radium Corporation,
Orange, N. J.,
October, 1921.

PHYSICAL CHARACTERISTICS OF NORMAL AND ABNORMAL EARS.

BY JOHN P. MINTON.

SYNOPSIS.

Sensitivity Curves for Normal and Abnormal Ears.—Previous investigators have worked only with normal ears and their results are not as a rule corrected for the resonance properties of the diaphragms used. Lord Rayleigh's curves are more reliable but do not extend above 768 double vibrations. In the present work a telephone receiver was used with a natural frequency above the range of the tests, 5,200 d.v., and its vibrational and electrical characteristics were determined so that the vibrational energy of the diaphragm could be calculated for any current of any frequency used. The currents were generated with an audion oscillating circuit, and a Wheatstone bridge was used in measuring the minimum audible current for both normal and abnormal ears; the readings in the case of normal ears were then converted into *minimum vibrational energy* and plotted *as a function of the frequency up to 4,000 d.v.* Curves are given (1) for normal ears; (2) for ears diseased only in the middle ear; (3) for ears diseased only in the internal ear; (4) for ears having a combination of middle and internal ear trouble. The normal ear curve shows a number of characteristic maxima with subsidiary inflections. In *middle ear deafness* the hearing is most deficient for low tones and more nearly normal for high ones, while *inner ear deafness* begins for high pitches and may not affect the hearing for low pitches. Sets of curves show the development of the diseases with time. In true *nerve deafness* cases have been studied in which total deafness appears to exist for a part of the sound spectrum; in one case on record, for instance, 200 billion times the energy required to stimulate the normal ear failed to produce the sensation of sound. Some *conclusions regarding the mechanism of audition* are drawn. The normal ear acts like a complex mechanical or electrical vibrating system whose response depends on many factors including the tympanum, bones, muscles, ear cavities and the internal ear. No resonant frequency can be assigned to any one member of it. When the middle ear mechanism is absent, the internal ear has resonant frequencies different from those of normal ears. The receiving mechanism in the internal ear is arranged in a linear manner beginning with the basal part which probably responds to the high pitched sounds, and each section is sensitive to only a narrow range of frequencies. The probable fact that the high frequency fibers are under greater tension than the lower frequency ones may account for the characteristics of internal ear deafness.

Discussion of Theories of Audition.—The difficulties confronting each theory are briefly pointed out. In some ways the above results tend to confirm the Helmholtz theory, but it is hard to see how any mechanical theory can explain the absolute insensitiveness to a limited range of pitch which has been observed in cases of nerve deafness.

I. INTRODUCTION.

THE present work was undertaken in coöperation with Dr. J. Gordon Wilson, Head of the Department of Otology at Northwestern University Medical School. Through this coöperative study much light

has been thrown on the subject of deafness and on the manner in which the normal ear functions. In the present paper are given some of the physical data on normal and abnormal ears, together with a discussion of the theoretical bearing of these data from the viewpoint of the theories of audition.

Inasmuch as the present method of testing involves the use of telephone receivers, it will be well to refer briefly to the work of other investigators who have published results on normal and abnormal ears. Rayleigh has summarized[1] somewhat briefly the early results on the minimum audible current in telephone receivers obtained by Preece, Tait, De la Rue, Brough and Ferraris. Rayleigh found difficulty in harmonizing the results obtained by these investigators with those secured by himself.[2] However, this lack of agreement is not to be wondered at in view of our present knowledge of telephone receivers and particularly in view of the diverse conditions under which the experiments were made.

The early work in this field did not extend above 768 d.v. (double vibrations), so that the sensitivity of the ear could not be estimated over the whole region of frequencies which are necessary for both speech and musical sounds. Rayleigh in his early experiments found a maximum of sensitiveness to receiver-currents in the region of 640 d.v., but he recognized that his data were insufficient to warrant the drawing of this conclusion. It is of interest to note that Rayleigh's maximum corresponds to the position of the first maximum of sensitiveness of some of the curves for normal ears shown in the present paper.

In 1902 Wien[3] published the results of his researches in which he used different types of receivers. The difficulty with these, as with earlier results which were obtained with telephone receivers placed against the ear, was that the ear-characteristics were masked by those of the receiver. Doubtless, the natural frequencies of Wien's receivers when in contact with the ear were in the region of 1,200 d.v. and we should expect the maxima in his curves to occur in this region, as they do. Furthermore, when receivers are used much above their natural frequencies the response of the diaphragm is of a rather complicated nature which cannot well be taken into account and corrected for.

Rayleigh[4] again attacked the problem of the sensitiveness of the ear

[1] Lord Rayleigh, "On the Minimum Audible Current in The Telephone," Phil. Mag., 38, pp. 285–295, 1894; Scientific Papers, Vol. IV., pp. 109–118.

[2] Loc. cit., 1.

[3] M. Wien, "Über die Empfindlichkeit des menschlichen Ohnes für Töne verschiedener Höhe," Pflüger's Arch., 97, p. 1, 1903; Physik. Zs., 4, pp. 69–74, 1902; Winckelmann's Handbuch der Physik, Akoustik, p. 248.

[4] Lord Rayleigh, "On the Relation of Sensitiveness of the Ear to Pitch, investigated by a New Method," Phil. Mag., Vol. 14, ser. 6, pp. 596–604, 1907.

by an entirely different method which depended upon the use of the principle of dynamical similarity.[1] Although his results extended from 85 to 512 d.v. they are of considerable interest in that the variation between these two frequencies was much less than that found by Wien. This difference is probably entirely accounted for by the fact that Wien was not able to correct for the receiver-characteristics. The present data agree with Rayleigh's, in the manner shown by the two curves in Fig. 1. The ordinates are arbitrary units of condensations in the case of Rayleigh's data and arbitrary units of current through a receiver tuned to 5,215 d.v. in the case of the present data. The present results are for a particular ear, while Rayleigh's are a mean of several tests on different people. The differences between the two curves are easily explained by the fact that the present data are threshold values while Rayleigh's are "just above" the threshold. Then too, fatigue-effects were completely eliminated in the data taken by the writer.

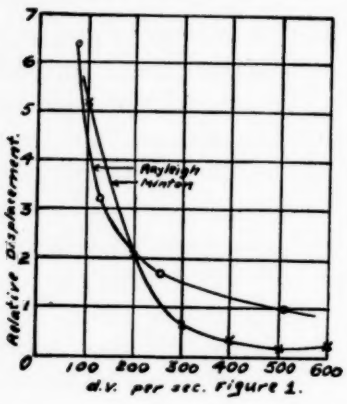


Fig. 1.

Recently Kranz[2] has published results on the sensitiveness of normal ears. In these tests he made use of the thermophone.[3] While this device has no resonance of the ordinary type, it does not give sufficient sound intensity for the purposes of these tests on normal and abnormal ears.

Seashore, Dean and Bunch [4] have carried out extensive tests on normal and abnormal ears by means of their audiometer and an ordinary telephone receiver. However, in the region between 500 and 3,500 d.v. they have been unable to decrease the current in the receiver below the threshold value. For this reason their work is not of importance from the viewpoint of sensitiveness of the ear at various frequencies. Their work is of a clinical nature and is designed to assist in devising an apparatus for the diagnosis of deafness.

The present work, then, was undertaken with the hope of avoiding difficulties encountered by other investigators and, therefore, with the

[1] Lord Rayleigh, Theory of Sound, Vol. II. (§§ 381).

[2] F. W. Kranz, "Minimum Sound Energy for Audition," PHYSICAL REVIEW, p. 384, March 1921.

[3] H. D. Arnold and J. B. Crandall, Thermo-phone, PHYSICAL REVIEW, Vol. 10, pp. 22–38, 1917.

[4] Seashore, Dean and Bunch, "The Audiometer in the Otological Clinic," Am. Otological Soc., Vol. 15, Part II., pp. 36–60, 1920.

hope of securing more trustworthy data on normal and abnormal ears tested over the region of frequencies which is important for speech and for musical sounds.

II. EXPERIMENTAL PROCEDURE.

The present method of testing the sensitivity of the ear, or the degree deafness, consists in determining the minimum audible current, produced by an audion oscillator, at various frequencies through a telephone receiver tuned to a natural period of 5,215 d.v. With these current-readings and with the electrical and vibrational characteristics of the receiver determined by standard impedance analysis,[1] the vibrational energy at the various frequencies of the receiver diaphragm may be calculated. The sensitivity of the ear may be defined as the reciprocal of the vibrational energy of the receiver. This energy can be calculated with considerable certainty provided the receiver is not used above its natural period.

Figure 2 shows a diagram of the testing circuit [2] which has been used

[1] Numerous articles by Kennelly and his co-workers are published in Am. Acad. of Arts and Science, Proc. Am. Phil. Soc., and in the Proc. Inst. Radio Engineers.

The velocity, v, of the receiver diaphragm can be calculated from the following formula which has been used frequently in telephone receiver theory:

$$v = -\frac{\omega_0 \sqrt{Z_m r}\ \sqrt{X_d^2 + (R_d - R_0)^2}\, i}{\sqrt{r^2 + \left(m\omega - \frac{s}{\omega}\right)^2}\ \sqrt{X_{df_0}^2 + (R_{df_0} - R_0)^2}}.$$

where $\omega_0 = 2\pi f_0$; f_0 = the natural frequency of the diaphragm.
$\omega = 2\pi f$; f = the frequency (d.v.).
Z_m = maximum motional impedance.
r = mechanical resistance.
m = effective mass of the diaphragm.
s = elastic coefficient.
X_d = damped reactance (variable frequency).
R_d = damped resistance (variable frequency).
X_{df_0} = damped reactance at the natural frequency.
R_{df_0} = damped resistance at the natural frequency.
R_0 = direct current resistance.
i = the minimum audible current.

All these quantities should be expressed in c.g.s. units in order to have the velocity expressed in cm. per second.

The displacement of the diaphragm at various frequencies is given by the equation $x = v/\omega$. The effective mass of the diaphragm (it is considered that the diaphragm curvature is a (cosine)^2 curve) in the case of the high natural period receiver was calculated to be 0.375 gram. The velocity, v, calculated as above, is that of this effective mass (.375 gram) of the diaphragm. The effective vibrational energy of the diaphragm is then given by $1/2mv^2$. The sensitivity, then, is taken to be, in the present work, the reciprocal of this minimum vibrational energy.

[2] This method of measuring the minimum audible current has been used in the past by the Western Electric Co. It was also used and published by E. W. Washburn, "The Determination of the Audibility Current of a Telephone Receiver with the Aid of a Wheatstone Bridge," Proc. Inst. Radio Engineers, pp. 99–109, Vol. 6, 1918.

in this work. The receiver, R, is held against the ear with a constant force by means of a light head band. The oscillator is set for a definite frequency and the current flows through the bridge circuit composed of

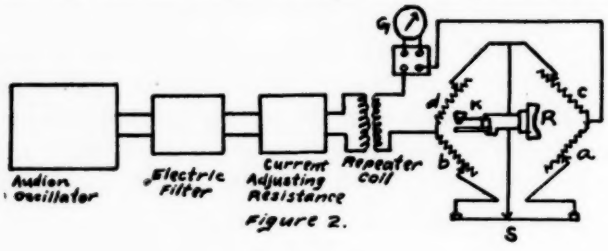


Fig. 2.

non-inductive resistances and the receiver. The resistances c and d are held constant while a, b and the slide wire, S, are adjusted for the threshold values of the minimum audible current. The key, K, is provided so that the patient may operate it intermittently and thus avoid fatigue-effects completely. The minimum audible current can be calculated from well-known formulæ when the values of a, b, c, d, S, the impedance of the receiver, R, and the current through the galvanometer, G, are known.

Two types of curves are shown in the present paper. The first type shows how much current is required for the patient to hear as compared with that required by the ear which had been selected as a normal reference ear. These curves of relative receiver-currents at the various frequencies were taken with the aid of a small receiver placed on a light head band which was of a standard type. The second type of curves shown gives the absolute sensitivity of the ear at the various frequencies. These curves were obtained from those of the first type together with the absolute sensitivity curve of the normal reference ear. This last curve was determined by means of a special telephone receiver tuned to a natural period of 5,215 d.v. The electrical and vibrational characteristics of this special receiver were determined by impedance analysis, and the energy at the various frequencies of the diaphragm was calculated from a formula well known in receiver-theory.

As Rayleigh has pointed out,[1] the resonance of the external auditory canal is materially altered by placing a receiver against the ear. However, tests which have been made show that the maxima of sensitivity for the normal reference-ear (Fig. 3) come at the same positions when the external canal is filled by a soft rubber plug with a small hole through it which connects the drum to the receiver by a small air column. Thus

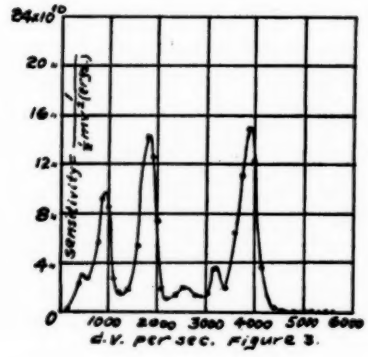
[1] Loc. cit., 4, p. 598.

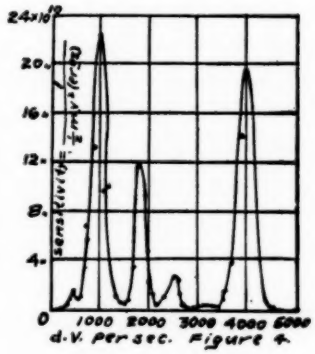
it is fairly certain that, as far as the present tests go, it is not so much in the introduction of resonance in the external ear as in the elimination of such a possible resonance that objection might be raised. The answer to such an objection is that the curves represent the vibratory characteristics of the ear itself, excluding possible air-chamber resonance. This is precisely what is desired in a study of the nature attempted here.

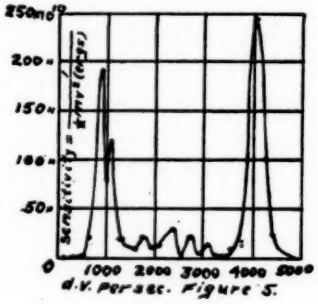
No question can be raised, I think, as to the accuracy of the results herewith reported. Tests made on normal ears over a period of two years check on the average to within about five per cent. Tests on patients, especially on some children as young as five years, have been checked from time to time to an altogether surprising degree.

III. EXPERIMENTAL RESULTS.

Sensitivity of Normal Ears.—Figures 3, 4, 5 and 6 represent the variations that are found among normal ears; that is, ears in which no known







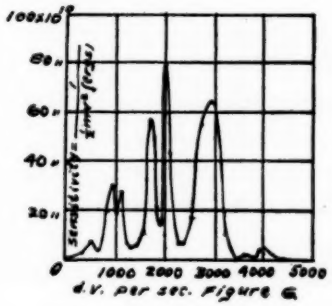


Fig. 3. Fig. 4.
Fig. 5. Fig. 6.

physiological defects exist. The first two curves are the right and left ears of a person 34 years old, the curves in Fig. 5 and 6 are for different persons 23 years old. As already stated, the ordinates represent the

reciprocal of the vibrational energy of the receiver diaphragm whose natural period was 5,215 d.v. The ordinates are probably proportional to sound energy, but more will be said on this phase of the subject later. The total sound energy produced by the diaphragm is probably not more than two per cent. of the vibrational energy.

The curves are seen to have distinct maxima which resemble in all respects the resonant frequencies of coupled mechanical or electrical systems. There are several maxima of much smaller magnitude in each of the curves. These curves have been checked from time to time, so that the smaller maxima are unquestionably present and are not due to observational errors.

At the threshold of audition, then, there exists a wide variation among normal ears and each ear possesses well defined maxima at particular frequencies. We may refer to these maxima as resonant frequencies for they show definitely that from a mechanical point of view we may think of the ear as a whole as a complex coupled vibratory system. A mechanical system of this nature possesses well-defined resonant frequencies whose positions and magnitudes are determined by the various inertial, elastic, dissipational and coupling coefficients. *The normal ear may unquestionably be thought of in exactly the same way, the various air cavities of the ear being considered as parts of the system.*

Sensitivity of Abnormal Ears; Middle Ear Deafness.—The six curves shown in Figs. 7 to 12 inclusive are typical examples of those which are obtained for middle ear defects. These curves are comparisons with the normal reference ear (Fig. 3) which was selected for this purpose since it was about an average of the normal ears. In studying these comparative curves one should keep in mind the sensitivity curve for the reference ear and should also bear in mind that these curves are for the threshold of audition only. If the sound intensity is proportional to the vibrational energy of the diaphragm, then the squares of these relative receiver currents give a direct comparison of the sound intensity just necessary for audition for abnormal ears compared with normal ears.

Figure 7 gives the curve for an ear having an abnormally thin drum membrane surrounding the tip of the maleus where it is attached to the center of the drum. Figure 8 is for an ear whose drum is indrawn from its normal position until the tip of the maleus is touching the rear wall of the middle ear cavity. Figures 9 to 12 inclusive show curves for different patients whose defects are the same and is described by the word "otosclerosis" used by the medical profession. This lesion is often described as "fixation of the stapes" of the middle ear.

All six of these curves for middle ear deafness show interesting varia-

tions that exist in the degree of hearing possessed by individuals. Generally speaking, the depression below normal is greatest at the lower frequencies and the hearing becomes more nearly normal with increasing frequencies. There is, therefore, an increase in the elastic factors of the

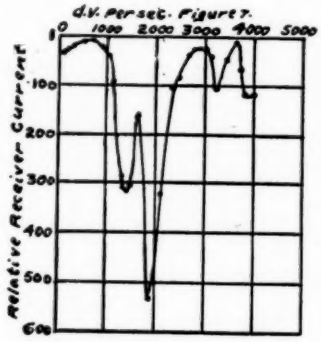


Fig. 7.

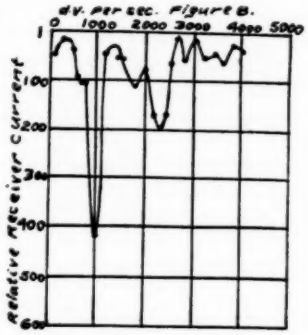


Fig. 8.

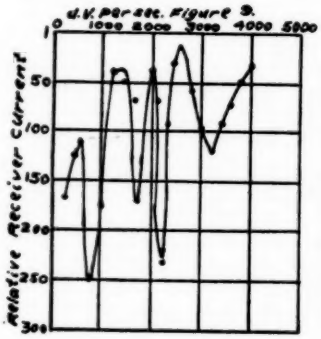


Fig. 9.

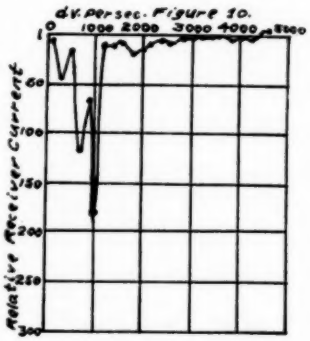


Fig. 10.

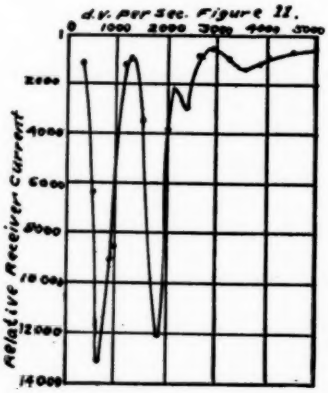


Fig. 11.

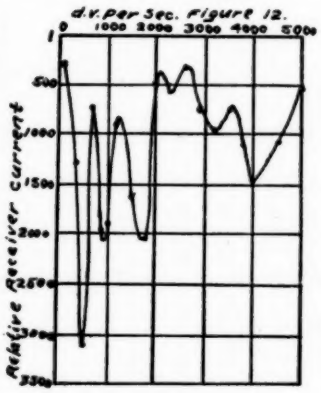
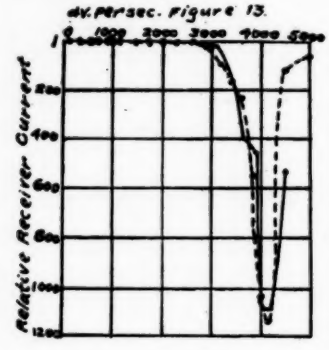
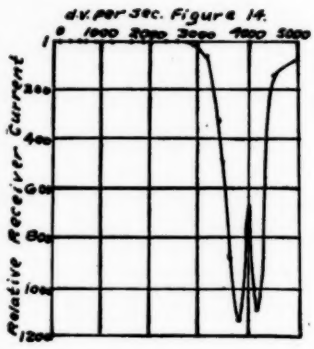
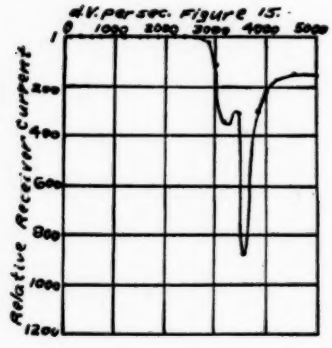


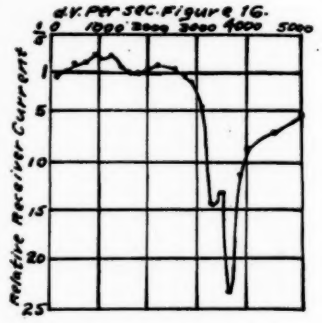
Fig. 12.

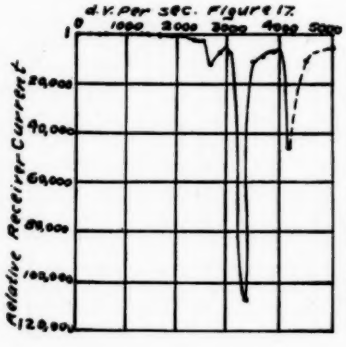
ear considered as a vibrational system. Other physical changes take place also for there is usually a depression in hearing at all frequencies as the curves show. The greatest depressions usually occur at frequencies corresponding to those of the maxima shown in figure 3; namely, from 700 to 1,000, 1,500 to 2,200 and from 3,500 to 4,000 d.v. So that sen-











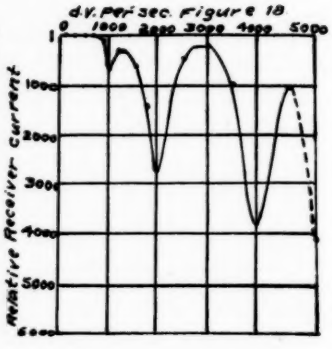


Fig. 13. Fig. 14.
Fig. 15. Fig. 16.
Fig. 17. Fig. 18.

sitivity curves for ears with middle ear defects are much alike among themselves and quite different from those obtained for normal ears.

Attention might be drawn to the sharp depression at 2,200 d.v. in Fig. 9. It was not expected, in view of the normal curve shown in Fig. 3, that this particular decrease in hearing would occur at this frequency. Near the threshold of audition the patient complained of the tone being quite noticeably impure. This did not occur at any of the other frequencies even though the depressions were large. This phenomenon was due to the presence of an internal-ear or nerve lesion which produced in the ear a subjective ringing (tinitus) whose pitch was approximately 2,200 d.v. For a loud receiver tone the patient was not conscious of the tinitus but for a weak tone the intensity of the subjective and objective tones was approximately equal and the patient was quite conscious of the effect produced by the existence of the two tones. So that superimposed upon the middle ear trouble is this internal ear or nerve lesion. The practical application of such information is at once apparent.

Internal Ear or Nerve Deafness.—The group of curves shown in Figs. 13 to 18 inclusive are for different cases of what is called "nerve deafness" by the medical profession. Figs. 13 and 14 are for the left and right ear, respectively, of one patient. Figs. 15 and 16 are for the left and right ear, respectively, of another patient. Figs. 17 and 18 are for different patients.

The dotted curve shown in Fig. 13 was taken about six months after the solid curve was obtained. The two curves are sufficiently alike to make it possible to say that no appreciable changes in the degree of hearing or in the region of the ear affected had occurred during the period of six months. The trustworthiness of the results is at once evident.

The characteristic of the type of nerve deafness which these curves represent is that the sensitiveness is normal at all the lower frequencies and starting at some definite frequency and including all higher ones the degree of hearing is seriously decreased. Thus, the nature of the lesion is such that it is confined to definite frequency limits. Over this confined frequency region, however, the sensitiveness decreases uniformly, reaching minima of sensitivity and then gradually increasing again. In other words, *there is no discontinuity between the affected and the unaffected region.* The location of the lesion in the ear for defects of these types could not be in the middle ear mechanism nor in the drum membrane, for, if such were the case, there would be obtained the types of curves shown in the group of six curves given in Figs. 7 to 12 inclusive. Thus, for these particular curves corresponding to nerve-deafness the vibratory mechanism of the middle ear is in normal condition. The lesion is con-

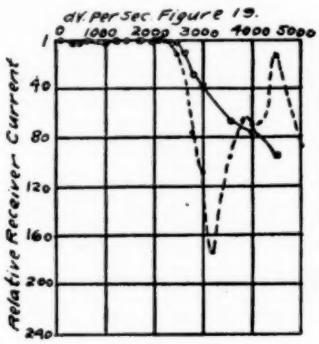
fined to the internal ear mechanism, or in the nerves, including their endings. Since the depressions in Figs. 13 and 14 are so nearly alike in position and magnitude, the question naturally arises as to whether the lesion might not be located at the center of perception itself. It is fairly certain that the question can be answered in the negative for numerous curves for cases of nerve deafness have been taken and practically all of them show that the disease has not affected both ears alike in magnitude and in many cases only one ear has been thus affected. In the example cited above, the agreement in magnitude of the depressions is to be looked upon merely as a coincidence, or that the disease has affected both ears alike. The depressions shown in Figs. 15 and 16 are very likely due to infection from diseased tonsils, but in the present article the medical side of the subject is not considered. Those interested in this phase of the subject may refer to a previous paper by Dr. J. Gordon Wilson and the writer.[1] It is of much theoretical importance, and is indeed surprising, that so great deafness, as for example that shown in Fig. 17, can exist at some frequencies and no deficiency at all appear at the lower ones. In passing it is important to state that with the exception of the last example (Fig. 18) there is not observable a very serious insensitiveness to speech sounds as used in ordinary conversation. The most important region for speech sounds is certainly below 2,000 d.v.

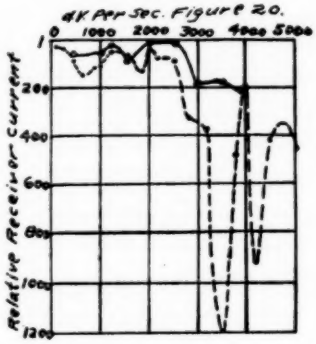
Time Development of Nerve Deafness.—The group of curves corresponding to nerve deafness, to which attention has just been called, show the different stages in the development of this type of deafness. The curves given in Figs. 13 and 14 and in 15 and 16 are for people about twenty-eight years old, while Fig. 17 is for a person about forty-five years old and Fig. 18 is for a person about sixty years of age. This type of deafness, then, becomes more acute and progresses toward the lower frequencies with time. To confirm this view, the curves shown in Figs. 19 and 20 are given. The time interval between the upper and lower curves in Fig. 19 was about eight months, whereas the time interval between the upper and lower curves in Fig. 20 was about thirteen months. The former curves for a case of nerve deafness in a person twenty-seven years of age are alike in sensitiveness at the lower frequencies but unlike at the higher frequencies. The latter curves (Fig. 20) are for a case of both middle and internal ear troubles and during the period of thirteen months a very serious increase has occurred in the extent and magnitude of the deafness for both the middle and internal ears.

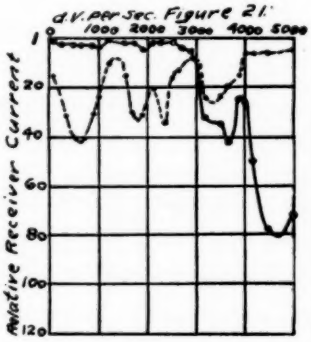
Special Cases and Combinational Defects.—Fig. 21 is interesting in

[1] John P. Minton and J. Gordon Wilson, "The Sensitivity of Normal and Defective Ears for Tones of Various Frequencies," Proc. Institute of Medicine of Chicago, 1921.

that it shows that the type of deafness may be quite different for the two ears of the same patient. The curve marked with the circles is for the ear having an internal ear or so-called "nerve" lesion while the one indicated by the dots is a typical curve for middle ear deafness. The "nerve" lesion is probably traceable to nose and throat infection.







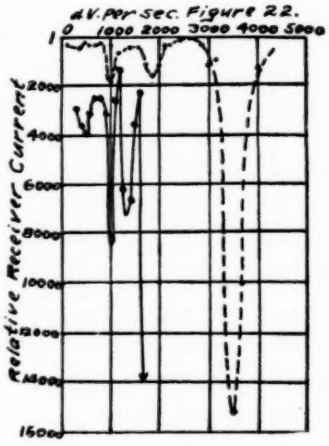


Fig. 19. Fig. 20.
Fig. 21. Fig. 22.

Fig. 20 has already been referred to as representing a combination of middle and internal ear lesions. The curve drawn through the circles indicates internal ear trouble which apparently includes the whole range tested. There is also a suggestion of middle ear trouble in the upper curve, but the lower curve clearly indicates the presence of both a middle and internal ear lesion.

The curves shown in Fig. 22 are quite interesting; the upper one being for the left ear while the lower one is for the right ear of the same patient. The drum membrane, ossicle bones, and tensor and tympanic muscles

are absent in the left ear. Hence, the sensitiveness of the ear due to the sympathic vibrations of these absent members is gone and, therefore, there are three maxima of depression in hearing relative to the normal reference ear (Fig. 3). It is significant that the depressions come exactly in the same localities in which the peaks occur in the normal reference ear. These absent members are, then, almost certainly responsible for the presence of the maxima of sensitivity in normal ears. The large depression below normal at 3,500 d.v. is most probably due to a combination of both middle and internal ear trouble. There is evidently here a true partial nerve deafness for at 2,600 d.v. the hearing was practically normal and from vibrational or mechanical defects alone we could hardly expect such large depressions in hearing on both sides of 2,600 d.v.

The right ear, shown by the lower curve, has the drum membrane and the middle ear mechanism present. Deafness is much more marked in this ear than in the left one. Bone conduction and, therefore, the hearing due to the internal ear and auditory nerves, as tested by length of time the patient could hear vibrating tuning forks placed against the mastoid bone, was equivalent to that of a normal ear up to about 1,200 d.v. or perhaps somewhat higher. Thus the presence of the drum membrane, ossicle bones, stapes, etc., in the middle ear are a hindrance in this case to good hearing rather than an aid to it. Between 1,600 and 1,700 d.v. something amounting to a discontinuity has occurred. The relative receiver current was made 75,000 at 1,700 d.v. and nothing whatever could be perceived. No tones above 1,600 d.v. were heard although the vibrational energy of the receiver diaphragm was maintained at about 5×10^9 times as large a value as is required for audition by normal ears. Thus, we have here a case of what is probably total deafness due to a lesion lying within the nerves including their endings. This curve, and others like it, bring out as clearly as one could wish the sharp distinction between vibrational and true nerve deafness.

IV. Theoretical Aspects of the Present Data.

There has been proposed no theory of the mechanism of audition that has been fully accepted by the various groups of men interested in this field. Helmholtz's[1] basilar membrane resonance theory of the manner in which the ear may be thought of as functioning has not been accepted and is meeting with more and more opposition as further data are collected. Nevertheless, his central idea of the analysis of sounds into the various simple harmonic waves of which they are composed has remained as a fundamental proposition in thinking of the phenomena of audition.

[1] Helmholtz, Tone Sensations.

Shambaugh [1] has rejected Helmholtz's theory and has substituted for it a similar one based on the tectorial membrane vibrating in the manner postulated by Helmholtz for the basilar membrane. The objections urged against Helmholtz's theory may be urged even more strongly against the tectorial membrane theory. Wrightson and Keith [2] in their coöperative study of the ear have rejected the resonance theories of audition and have substituted for them a non-resonant theory of the action of the ear as a whole. It appears, however, from a recent discussion [3] of this theory by the members of the Royal Society of Medicine that there are numerous objections to the Wrightson-Keith theory. Other theories of audition [4] have been proposed, but they will not be referred to here inasmuch as they have not survived the criticism brought against them. The question arises, what bearing do the data reported in the present paper have upon existing theories of audition and do they suggest any modification in these theories?

The general answer to these questions is that this work does show quite definitely in some respects at least how the ear functions. In the first place, it functions as though it were a complex vibratory system, consisting of the drum membrane, the chain of ossicle bones, the tympanic muscles, the internal ear and finally the external and middle ear cavities. The response of this system as measured by the sensitiveness of the ear at various frequencies is exactly of the type that is obtained for an ordinary coupled mechanical system. The resonant frequencies of such a system occur at places controlled by the coefficients which define the system and no resonant frequency can be assigned to any one member of it.

Second, the curves taken on patients who have the drum membrane and the middle ear mechanism absent seems to suggest that the internal ear itself has well-defined resonant frequencies which are located at different places from those of normal ears. A further study of ears of this nature will be of much fundamental importance and it seems best to withold further comments on the vibratory nature of the internal ear until more data are available.

In addition to this mechanical-vibratory functioning of the ear there is a second important mode of operation as the data amply show. In the section on experimental results attention was called to the extremely

[1] George E. Shambaugh, The Laryngoscope, July, 1909, Annals of Otology, Sept., 1910, Dec., 1910.

[2] Wrightson-Keith, An Analytical Mechanism of the Internal Ear.

[3] Royal Soc. Medicine; Section on Otology, discussion March 21, 1919; also The Journal of Laryngology and Otology, Feb., 1921, Vol. 36, No. 2.

[4] Bonnier: Journal de Physique, p. 578, 1906, Theories de L'Audition.
Stefanni: Il Nuovo Cimento, Vol. 61, 1915, La Percezione der Suoni.

sudden and surprisingly large variations in the degree of hearing for the cases of internal ear troubles. Such large variations would not be observed for defects of a purely vibratory nature. The deficiency in hearing due to these internal ear lesions extends over bands of frequency, that is, over a series of consecutive frequencies which cover a range of from one hundred or so double vibrations to as much as several thousand vibrations. In some cases the degree of hearing is equivalent to normal up to about 1,300 d.v. and then within one hundred d.v. it may be so greatly depressed as to amount to total deafness for all the higher frequencies. Again, the hearing may be greatly depressed and then for a small range of frequencies be practically equal to normal, and then with increasing frequency it may suddenly decrease to a very low value. These and other data show, first, that the internal ear is laid out in a linear manner. That is, that part of the internal ear which produces the sensation of low frequency notes is in one section of the ear and the adjacent section produces the sensation of a somewhat higher group of tones. Each succeeding section produces in turn the sensation of higher and higher notes. This view corresponds to that first put forth by Helmholtz and is also in agreement with the present ideas held by otologists. This view is further confirmed by the fact that in advanced stages of "fixation of the stapes" the disease enters the internal ear and affects first the high frequency sounds. This suggests that the basal part of the internal ear responds to the high frequency sounds, while the sections further and further removed from the basal part respond to lower and lower frequencies. Now, in a purely coupled vibratory system it is impossible to greatly affect one member without affecting the response of the system as a whole at all frequencies. For these reasons such defects as have just been described can not be due to middle ear trouble, but are probably due to those parts of the internal ear that have to do with one frequency or with a very narrow group of frequencies. That is, these defects are due either to the fibers of the basilar membrane or to the nerves, including their endings. The extremely sudden depressions in hearing, amounting in many cases to total deafness, are certainly cases of nerve trouble. The gradual depression in hearing for the higher frequencies cannot be called nerve deafness without considering the subject further. This discussion leads us to the rôle played by the basilar membrane.

Let us assume that the shortest fibers of the basilar membrane respond best to the highest frequencies, that the somewhat longer fibers respond best to somewhat lower frequencies, and so on until we arrive at the longest fibers which respond best to tones of the lowest frequencies.

Since the length of the longest fibers is but two or three times that of the shortest ones, in order that the assumption may hold, it seems necessary that the tension in the fibers increase rather rapidly with the decrease in their length. If this be true, then, for purely mechanical reasons the fibers may be expected to give way first over all the high frequency region because of the comparatively large tension in the fibers which cover this region. Hence, we may expect the sensitivity for tones of the highest frequencies to be lost sooner than for tones of the lowest frequencies. We may also expect that, as time goes on, the disturbance will travel in the direction of lower frequencies and become more and more acute for the higher ones. For this sort of a condition, which is not of the nature of a disease, we should expect to obtain the type of curves shown in Figs. 13 to 18 inclusive. From the point of view here considered, then, this type of so-called "nerve-deafness" is not nerve-deafness at all, but is rather a special type of vibratory deafness caused by the peculiar construction of the basilar membrane. True nerve-deafness would show itself by a sudden depression in hearing amounting in some cases to a total discontinuity in the curves. It should be borne in mind, however, that much additional data must be collected before such a theory can be very positively advanced.

The bearing of the foregoing experiments upon the Helmholtz theory of pitch perception is most clearly seen from a consideration of Fig. 17. It will be seen from a glance at this figure that at a frequency of 3,300 d.v. the current required to excite audition was about 110,000 times that required by the normal ear, while in the whole frequency region below 1,200 d.v. the patient's hearing was normal. The relative *energies* corresponding to the current-ratio, 1 to 110,000, is approximately 1 to 10 billion. In other words, it was possible in the case of this patient to apply in the frequency region of 3,300 d.v. an energy 10 billion times as much as corresponds to normal hearing at this frequency without stimulating in the slightest degree the sensation of hearing in the region below 1,200 d.v. where the patient's hearing was practically normal. Now in the Helmholtz theory, pitch perception is due to the coincidence of the impressed frequency with the natural frequency of the fibers of varying length and tension which constitute the basilar membrane. It is, however, extremely difficult to see how a mechanical system such as that represented by the basilar membrane with its fibers and attached Corti's arches could possibly receive ten billion times the normal energy at a given frequency like 3,300 d.v. without imparting as much as a billionth of that energy to the adjacent fibers which corresponds to vibration frequencies below 1,200 d.v. If these latter fibers had in this

case been thus forced into response with a billionth or even a hundred billionth of the incident energy the patient would have had the sensation of hearing in the region below 1,200 d.v. as can be seen easily by a reference to Fig. 3. If these considerations are fatal to the Helmholtz theory, there appears to be no alternative at present but to make pitch perception a property of the nerves themselves, including their endings, without attempting to find a mechanical explanation. This amounts to nothing more than the assertion of our inability at present to obtain a satisfactory mechanical basis for pitch perception.

In conclusion, the writer wishes to take advantage of this opportunity to express his appreciation for the continued interest and the very helpful suggestions received from Professors Millikan and Lunn throughout this work.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
July, 1921.

THE EFFECT OF OXYGEN AND HYDROGEN ON THE EMISSION OF ELECTRONS FROM HOT PLATINUM.

BY LAURICE L. LOCKROW.

SYNOPSIS.

Thermionic Emission from a Platinum Filament.—Previous observers have reported such conflicting results as to the effect of gases on the emission that a series of 20 tests were carried out by the author to determine the cause of these discrepancies. A tube with a long cylinder surrounding a V-shaped filament was found to give results more free from saturation difficulties, but even with it complete saturation could not be obtained, due perhaps to the presence of heavy negative ions. (1) *The effect of oxygen and air* on the emission was found to be to decrease it slightly, in agreement with the observations of Richardson, H. A. Wilson and others. This effect is temporary and is not due to the formation of heavy ions; and while it may accompany the formation of an oxide of platinum, no evidence for this was obtained. (2) *The effect of hydrogen* on the emission from pure platinum is probably nil. For in those cases in which the hydrogen causes a "permanent increase," that is an increase which remains after the removal of the hydrogen, the author's tests indicate that the effect is due to grease or oil vapor, although the hydrogen may hasten the action; and the large "temporary increase" usually observed when hydrogen is admitted is found to disappear upon heating the filament a long time in air and hydrogen, and hence is probably due to the action of hydrogen not on the platinum itself but on impurities contained in the filament. (3) *Richardson's constants for pure platinum* were found to be: $A = 9{,}900$; $b = 52{,}000$. These values are lower than those obtained by others and are subject to errors inherent in the resistance method of measuring temperatures. (4) *The thermionic work function for platinum* computed from the value of b comes out 4.46 volts as compared with 4.80 volts obtained by Koppius for the corresponding photo-electric function.

CONSIDERABLE material dealing with the emission of electricity from hot bodies has been published, so the writer will not go into a discussion of the general aspect of the problem in hand. Those to whom the subject is not familiar are referred to the several sources of information mentioned below.[1]

The effect on the emission of changing the filament temperature and the anode voltage has been well determined. The effect of gases has not been as well worked out. The writer hopes to point out in this paper several ideas in connection with the effect of gases on the emission of electrons from hot platinum.

From the results of experiments published in 1903, Dr. H. A. Wilson[2]

[1] "The Emission of Electricity from Hot Bodies," O. W. Richardson. "The Electrical Properties of Flames and Hot Bodies," H. A. Wilson.

[2] Phil. Trans., A, 202–243–1903.

concluded that the negative leak of electricity from a hot platinum wire in air, nitrogen or water vapor is independent of the gas pressure unless ionization by collision occurs and is approximately the same as the negative leak from the wire in a good vacuum. He also concluded that the negative leak in hydrogen is much larger than that in air or in a vacuum and that at low pressures it is very nearly proportional to the pressure of the hydrogen. O. W. Richardson [2] found that in certain cases the current in hydrogen was independent of the pressure over the range of 1 to 0.001 mm. Wilson later found [1] that in certain cases the leak was independent of the pressure over a range of 200 to 0.001 mm. He also found the leak with new wires to be a function of the gas pressure, but after the wires had been subjected to considerable heating in hydrogen the leak usually became independent of the pressure.

Langmuir[2] concluded from his experiments on tungsten that hydrogen permanently lowered the current, especially at low temperatures. He suggested that "oxygen would have a similar effect on the thermionic current from platinum that nitrogen has on tungsten. In other words, the oxygen would cut the thermionic current down to a value lower than the normal vacuum current (by the formation of an oxide). Hydrogen would reduce the oxide and allow the normal vacuum current to flow. Of course it is quite possible although not probable, that some gases may increase the thermionic current instead of decreasing it."

Due to these conflicting ideas the problem was again taken up. It was found that oxygen decreased the leak slightly and that after the platinum had been purified by heating for a long time, alternately in hydrogen and air, the hydrogen had no effect on the current. The results of these experiments led to an explanation of the results obtained in the previous cases.

APPARATUS AND METHODS.

In the experiments two types of tubes were used, designated as the old tube and the new tube. The old tube was made with two filaments hung vertically as shown in Fig. 1. By using two filaments both could be freed from gas by connecting in series and heating before a test. During a test the one was heated, furnishing the electrons and the other was cold, serving only as the anode. All filaments were of "chemically pure platinum," 0.25 mm. diameter and 8 to 10 cm. long.

The old tube required a fairly high voltage for saturation and ionization by collision occurred so as to hide the true effect of the gas. No difficulty from gases occluded in the metal parts was experienced. Ac-

[1] Phil. Trans., A, 208–247–1908.

[2] PHYS. REV. 2–450–1913.

cordingly the new tube was made with a cylinder of platinum surrounding a V-shaped filament. The cylinder was about one cm. in diameter and 4 cm. long. The tube was arranged so as to minimize the leakage of current over the surface of the glass.

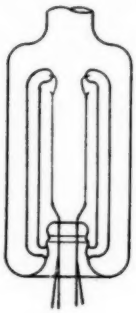


Fig. 1.

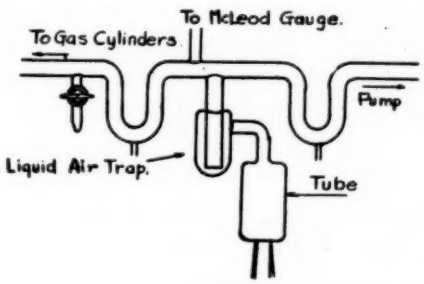


Fig. 2.

The apparatus was arranged as in Fig. 2. The system was exhausted by a Langmuir condensation pump backed by the usual oil pump. The pump could be cut off from the apparatus by a mercury column. The pressure was measured by a McLeod guage reading to about 0.00001 mm. The tube was separated from the remainder of the apparatus by a liquid air trap, and was placed as close to the pump as possible. In the first series of tests, the oxygen and hydrogen were stored in glass cylinders and were admitted to the apparatus through capillary tubes having stopcocks arranged to admit only a small amount of gas each time. The hydrogen was prepared from a solution of sodium hydroxide acting on aluminum. The oxygen was obtained from an "Oxone" generator. Both gases were purified by bubbling through a strong solution of potassium hydroxide and were dried over phosphorus pentoxide. A spectrum of a sample of the hydrogen excited electrically by a condenser discharge showed faint traces of nitrogen but no other impurity. A stopcock was provided to admit air. In the second series of tests hydrogen and air were the gases used. The cylinders were replaced by an electrically heated platinum tube by means of which hydrogen from a Kipp generator could be diffused into the apparatus. The air was admitted as before. A second mercury column was arranged to cut off the stopcock and the gas supply apparatus from the tube.

The filament temperatures were measured by the resistance method with the help of a Wheatstone bridge as shown in Fig. 3.

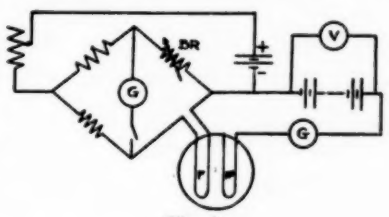


Fig. 3.

The Callender correction formula was used in the calculations. A correction for the cooling at the ends of the filament was made by assuming that 1 cm. of the total length of the filament has half the resistance of every other centimeter of the filament, so that for a total length of 8.4 cm., in the last series of experiments, the effective length was taken as 7.9 cm. The constants needed in the calculations were determined from readings at 0° C., 100° C., and 1066° C.

The thermionic currents were measured by means of a sensitive galvanometer provided with an Ayrton shunt.

EXPERIMENTAL WORK.

The experimental work was done in a large number of separate tests. From these, tests were selected as being typical. These are presented in the following material.

Test No. 1.—These early tests were performed with the old type of tube as described before. At the beginning of each test the tube was heated by a small electric furnace placed around it, to a temperature of about 350° C. The filaments connected in series were glowed out and the pumps were operated. The test was not started until the gauge indicated a pressure of about 0.00001 mm. Liquid air or solid carbon dioxide was kept on the liquid air trap.

A typical curve obtained with a new filament is shown in Fig. 4. The

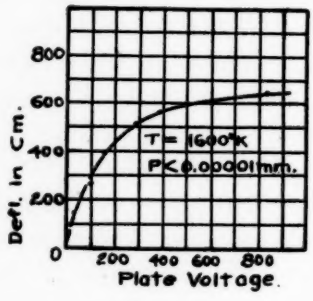


Fig. 4.

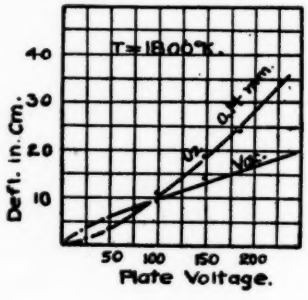


Fig. 5.

galvanometer deflection[1] due to the thermionic current is plotted against the plate voltage. It was found that this type of curve gave good indications as to the action of the tube and so was used throughout the remainder of the tests. In this case the current was large at a low temperature and was not easily saturated. This is characteristic of a new filament. The current decreased rapidly with time. Further heating with the pump operating and again in oxygen at low temperatures reduced the current to a low steady value which could be reproduced.

[1] One cm. deflection 5×10^{-8} ampere.

Test No. 2.—The current in oxygen as compared to that in a good vacuum is shown in Fig. 5.

The gas decreases the current to a small extent when the plate voltage is low. At the higher plate voltages the current is much larger than in a good vacuum. This increase in current is due to ionization by collision. Other tests were made with oxygen at pressures and temperatures respectively of 0.65 mm. and 1700° K., 0.56 mm. and 1830° K. with similar results. In every case the current returned to its initial value on removing the gas.

Test No. 3.—With a filament which had been in use for a time, curves were obtained as in Fig. 6. In a good vacuum the current did not saturate definitely and was a function of the temperature as well as voltage for low voltages at which the space charge relation should hold. This may be due to the presence of heavy charged particles in the emission or to the construction of the tube.

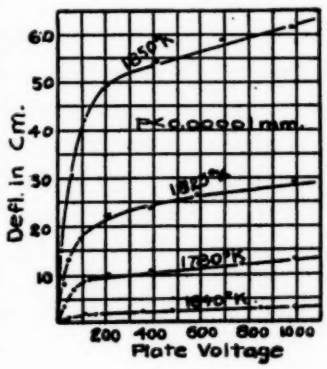


Fig. 6.

In the process of determining Richardson's constants for the above data, it was found that the points representing $\log i - \frac{1}{2} \log T$ plotted with $1/T$ did not lie on a straight line. However, by drawing a line representing as nearly as possible the coördinates, the following values were obtained:

$$A = 3{,}020,$$
$$b = 46{,}000.$$

Test No. 4.—Hydrogen at 0.55 mm. increased the current by a large amount at a temperature of 1710° K. The galvanometer readings are given below, contrasted with those obtained later in a good vacuum at the same temperature:

Plate Voltage.	Defl. with H_2.	Defl. in Vac.
10 volts	23.5 cm.	1.1 cm.
20	60	2.2
30	580	2.85
40	900	3.55

Further tests at this time with hydrogen gave erratic curves. The currents were large.

Test No. 5.—In hydrogen at 0.55 mm. pressure and at 1720° K. the

current was 14,000 units at 100 volts. Before admitting the hydrogen the current had been 8 units at 1710° K. and with the same voltage. The current did not return to its initial value upon removing the hydrogen. The curves were of about the same shape as before but the currents were much larger and were well saturated with the voltages used. At the higher temperatures the current began to fall off with time. For this "permanent effect" the following values of Richardson's constants were obtained:

$$A = 10^8,$$
$$b = 54{,}000.$$

Test No. 6.—The remaining experiments show that the permanent increase in current after heating the filament in hydrogen was really a secondary effect, and that there was a temporary increase in current which practically disappeared after working with the filament a long time. In these experiments the hydrogen was admitted to the apparatus by diffusion through the hot platinum tube.

The tube was heated and the filaments were heated in air. The tube was pumped out and solid carbon dioxide was put on the liquid air trap. Curves were obtained in hydrogen after heating in it at 0.0055 mm. for half an hour, after heating in it at 0.46 mm. for 5 minutes and again after heating in it at 0.51 mm. for half an hour. The temperature was 1630° K.

In every case the hydrogen caused a temporary increase in current. Upon removing the hydrogen the current dropped to a value comparable with its original value in a vacuum. There was a progressive decrease in the vacuum current throughout the test as is characteristic of a new filament.

Test No. 7.—The filament was heated in hydrogen at a pressure of 3 or 4 mm. at 1130° K. for 65 minutes. The hydrogen temporarily increased the current by a factor of 25 to 30 at low voltages. The currents after heating in the hydrogen are very nearly the same as those before as indicated in the following table:

Voltage.	Deflection of Galvanometer.		
	In Vac. before Heating in H_2	In H_2.	In Vac. after Heating in H_2.
15	0.40	8.7	0.40
30	0.75	18	0.85
160	1.10	33	1.25
120	1.32	64	1.40
200	1.50	220	1.60

Filament temperature 1680° K.

Test No. 8.—Hydrogen at 3 or 4 mm. pressure was allowed to remain in the tube 17 hours with no carbon dioxide or liquid air on the trap. At the end of this time the filament was found to be coated with a black deposit which slowly disappeared when the tube was heated and the filament glowed. Air was then admitted to about 7 mm. pressure.

A permanent effect apparently due to the hydrogen was found after letting the tube stand with hydrogen in it. The current in the hydrogen at 1680° K. was less than the current after pumping out at voltages below 350. The vacuum saturation current was 1,300 times larger than the small current obtained after heating in air for the same temperature. The current in air was somewhat smaller than the usual vacuum current at low voltages.

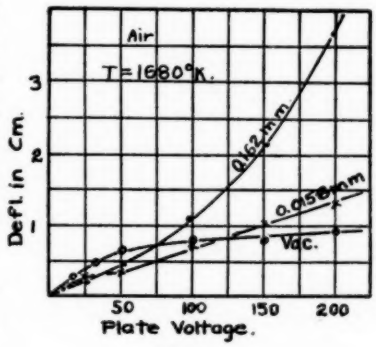


Fig. 7.

Test No. 9.—After heating the filament in air for a short time, the tube was exhausted. Air was admitted again with carbon dioxide on the trap and curves were obtained at pressures of 0.162 mm., 0.0158 mm., and in a good vacuum. These curves are given in Fig. 7.

The current in air was less than in a good vacuum at low voltages at which no appreciable ionization by collision occurs.

Test No. 10.—Hydrogen at 3 or 4 mm. pressure was allowed to stand in the tube for 10 hours with carbon dioxide on the trap. At the end of this time the gas was pumped out and a curve was obtained.

The current after the hydrogen had been removed was the same as before admitting it. That is, hydrogen had no permanent effect on the current when the liquid air trap was maintained at a low temperature.

Test No. 11.—This test was similar to No. 8. The tube was allowed to stand for 43 hours with hydrogen at 1/2 mm. in it. There was no refrigerant on the trap. At the end of this time the filament was found to be dirty in spots. The tube was pumped out. Upon heating the filament a grey deposit resembling finely divided mercury was driven from the filament to the walls of the tube. Upon heating the tube with the pump shut off, a pressure of 0.00097 mm. was recorded.

The hydrogen was again found to give a permanent effect when no refrigerant was used.

Test No. 12.—The apparatus was allowed to stand two days with air in it at atmospheric pressure. The pressure was reduced to 3 or 4 mm. and kept there the third day. All gas was then removed and the

filaments were allowed to stand for two days in the vacuum. The tube was then pumped out. The current was found to be small but it increased rapidly upon heating several minutes. After pumping out again after two hours, a large current was obtained. Heating in air brought the current back to its small value.

Test No. 13.—The tube and air trap were sealed directly to the pump. Mercury was put into the liquid air trap and was heated.

The mercury alone gave no permanent effect.

Test No. 14.—The current was measured and then hydrogen and mercury vapor were admitted, using the same apparatus as in the previous test. The filaments were heated for a short time. Upon pumping out the current was found to be small.

Mercury vapor and hydrogen gave no permanent effect.

Test No. 15.—A tube containing stopcock grease was sealed to the apparatus near the tube. The grease was heated and then after a few minutes the tube was freed from gas. The current was large but decreased slowly at high temperatures.

For the "permanent effect" produced by the grease vapor these values of Richardson's constants were obtained:

$$A = 9.70 \times 10^8,$$
$$b = 58{,}400.$$

Test No. 16.—The previous tests indicated that the permanent effect might even be produced in a good vacuum. To eliminate the permanent effect as far as possible air was admitted to the tube whenever left standing, and the filaments were heated in air for several hours before beginning the tests. The tube itself was also heated. Liquid air was used in these tests and it was not put on the trap until the pressure was down to about 1/2 mm.

The filament was kept at 1,800° K. and hydrogen was admitted in small amounts. The deflections of the galvanometer with 43 volts on the plate were as follows:

Pressure.	Deflection.	Pressure.	Deflection.
0.00001 mm.....	1.25 cm.	0.30	1.60
0.0001	1.25	0.36	1.65
0.057	1.40	0.44	1.80
0.09	1.50	0.49	1.90
0.15	1.50	0.69	2.00
0.25	1.60	0.0067.....	1.80

The slight increase in current in this test may be due to a real effect,

or, more probably, to the inability to maintain constant temperature. At any rate, the increase in current is small.

Test No. 17.—The new type of tube having a cylindrical anode was used in the remainder of the tests. With this type of tube the currents were fairly well saturated with 20 to 25 volts as compared to 100 to 200 volts for the previous type.

The following values of Richardson's constants were obtained with this type of tube after working with it a short time:

In a vacuum	$A = 300$	$b = 46{,}600$,
In hydrogen, $p = 0.0195$ mm.	$A = 1{,}230$	$b = 48{,}000$,
In hydrogen, $p = 0.0014$ mm.	$A = 795$	$b = 48{,}000$.

Test No. 18.—The filament was maintained at constant temperature and hydrogen was admitted to various pressures.[1]

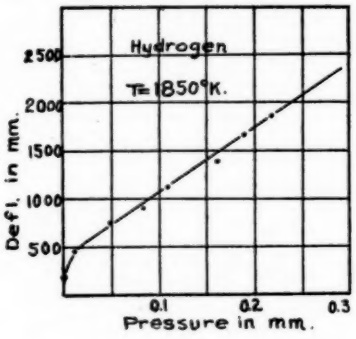


Fig. 8.

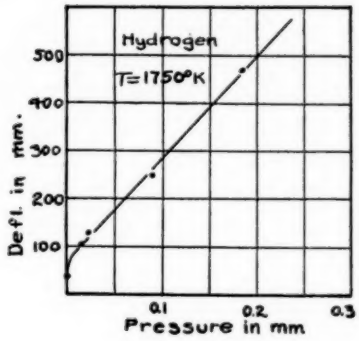


Fig. 9.

The results of the test are shown in Figs. 8 and 9, above. The current in the gas was found to be fairly well saturated as indicated by Fig. 10 below.

The deflection-pressure curves are straight lines except for the lower portion of the curves. These curves show the increase in current to be a linear function of the gas pressure provided the pressure exceeds a minimum value of about 0.01 mm.

The lead-in-wires of this tube were not very heavy and it was thought that there would be less error in temperature measurements with heavier leads. Accordingly the test was stopped, and another tube of the same type but with heavier leads was made.

Test No. 19.—The new tube gave a fairly large current at the start. Hydrogen increased the current by a large factor at first. This increase due to hydrogen fell off with time. The data was as follows:

[1] A change in the galvanometer was made. The new galvanometer gave 6.66×10^{-13} ampere per mm.

Gas.	Temperature.	Deflection.
Vac.	1800° K.	570 mm.
H_2 — 0.078 mm.	1800°	12,000
Vac.	1800°	660
Air.	1800°	———
Vac.	1800°	210
H_2 about 0.1 mm.	1900°	20,000
H_2 about 0.1 mm.	1800°	9,000
Vac.	1800°	300
H_2 1/2 mm.	1900°	15,000
H_2 1/2 mm.	1800°	3,200

The following values were obtained for A and b in a good vacuum:

$$A = 316,$$
$$b = 46{,}000.$$

Test No. 20.—The filament was heated for 5 or 6 hours alternately in air and hydrogen. After this heating the current in a vacuum was the same as in hydrogen within the limits of accuracy of the experiment. The current in air was slightly less than in a vacuum. The currents were well saturated as indicated by the typical curves in Fig. 11.

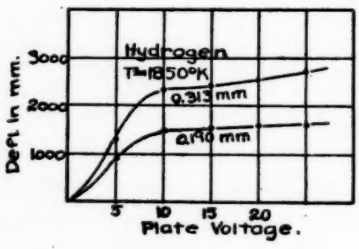


Fig. 10.

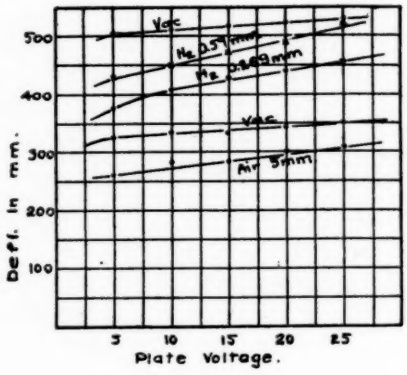


Fig. 11.

A summary of all the readings at 10 and at 15 volts are given in Table I. These voltages were chosen as being the ones at which the readings are typical.

Averages of these readings were made and for these, Richardson's constants were obtained as

$$A = 9{,}910,$$
$$b = 52{,}200.$$

TABLE I.

Summary of data for Test No. 20.

Temperature 1900° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.....		515	525
		475	485
		410	410
			350
		335	340
Air.....	5 mm.	280	290
		400	410
		355	360
H_2.....	0.0352 mm.	390	410
	0.0475	450	450
	0.098	470	480
	0.181	425	435
	0.269	410	425
	0.590	450	470

Temperature 1850° K.

Vac.....		255	265
		230	235
		210	210
			180
		180	180
Air.....	5 mm.	140	145
	0.266	175	175
H_2.....	0.0352 mm.	175	180
	0.0475	245	250
	0.098	240	245
	0.181	195	200
	0.269	195	200
	0.405	150	155
	0.590	235	245
	2	150	160
	3	165	180
	6	170	180
	8	175	180
	14	220	240

TABLE I. (*Continued.*)

Temperature 1800° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.....		115	120
		100	105
		90	92
			75
		73	73
Air.....	5 mm.	70	71
	0.226	74	76
	0.0186	76	77
H_2.....	0.0352	74	74
	0.0475	100	100
	0.098	104	105
	0.181	92	94
	0.269	90	92
	0.590	115	120

Temperature 1750° K.

Vac.....		61.5	63
		54	55
		45	47
			41
		42	43
Air.....	5 mm.	35	36
	0.226	46.5	47
H_2.....	0.0352	40	41
	0.0475	50	53
	0.098	51	52
	0.181	46	47
	0.269	44	45
	0.405	36	37
	0.590	58	61.5
	2	35	42
	3	33	34.5
	6	33.5	35.5
	8	39	41
	14	67	74

TABLE I. (*Continued.*)

Temperature 1700° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.....		26	27.5
		21	21.5
		17	18
			14
		14	14
Air.....	5 mm.	12	12
	0.226	15	15.5
	0.0186	13.5	14
H_2.....	0.0352	12	13
	0.0475	20	20
	0.098	17.5	18.5
	0.181	13.5	15.5
	0.269	13	14
	0.590	25	26
	14	23	27

DISCUSSION AND CONCLUSIONS.

The Normal Vacuum Current. Tests Nos. 1–3–17–19–20.—For convenience, the current in a vacuum after the filament has been heated in air or oxygen long enough to remove any surface impurity such as carbon, is designated the normal vacuum current. The normal vacuum current from a new filament is large and is not readily saturated. With further heating the current decreases and becomes more easily saturated. Heating alternately in hydrogen and oxygen hastens the decrease in current.

After working with the filament for a long time, there is still a difficulty of saturation. With the old type of tube the curves (Fig. 6) are not in accordance with the theoretical space charge curves. Since the voltage across the filament did not exceed 5 volts, it is not likely that the filament drop caused this departure. The failure to follow the space charge relation is probably due to the construction of the tube or the presence of heavy charged particles in the emission. With the new type of tube, the space charge relation could not be studied because the voltage for saturation was but very little larger than the filament drop. The failure to obtain complete saturation remained. With both types of tubes, the lack of complete saturation seems to be due to the presence of heavy charged particles in the emission.

The values of Richardson's constants for the normal vacuum current for filaments which had been used for some time are summarized below:

Test No.	A.	b.
3	3,020	46,000
19	316	46,000
20	9,900	52,000

The last pair of values are the most reliable to take as the values of Richardson's constants for pure platinum as they were obtained from the average of a large number of readings and after the filaments had been used a long time. They are, however, subject to the errors of the method of measuring the temperature and ought not be considered precision measurements. They are worthy of consideration as better than the usual qualitative measurements. Experiments in which the temperatures are measured by optical methods ought to be performed as a check.

From this last value of b, we get the work function, or the potential corresponding to the velocity of an electron necessary to let it escape from the metal as 4.46 volts. This is comparable to the value of 4.80 volts obtained by Koppius [1] as the work function for the photoelectric effect of platinum.

These values of A and b are both lower than those obtained by others. Quoting H. A. Wilson,[2] "For pure platinum in a vacuum or in air at low pressure O. W. Richardson, H. A. Wilson, F. Horton, Deininger and others have all obtained values of Q differing little from 130,000 ($b = Q/2 = 65{,}000$). As to A, however, there is a good deal of doubt, for a small error in the currents leads to a large error in A, and traces of hydrogen or other impurities change A much more than Q. It is probable that A for pure platinum is not much less than 10^8." The temperature scale may be different from that used in the previous experiments, so as to cause the difference in results. In the experiments described here, the effect of hydrogen has been eliminated as a source of error. The impurities which caused the temporary increase of current when hydrogen is admitted, as discussed in subsequent pages, have been eliminated. There may remain, however, other impurities.

The Current in Oxygen and Air. Tests Nos. 2–9–20.—The effect of oxygen was similar to the effect of air in the case of the old type of tube. The current in both cases was smaller in the gas than in the vacuum at the lower voltages. With the higher voltages the current was larger in the gas.

The tests with air in the new type of tube indicate a small decrease in current due to the gas. The tests with the new tube were not confused by ionization by collision and allow a definite conclusion.

[1] PHYS. REV., 17, 395, March, 1921.

[2] "El. Prop. of Flames and Hot Bodies," page 15.

The decrease in current may be due to the formation of an oxide of platinum on the surface, having a smaller emission than the platinum. If there is such an oxide, it is quite volatile because on removing the gas the current returns to its normal value. Langmuir proposed the idea of an oxide in connection with the effect of hydrogen. These experiments indicate that the formation of an oxide does not play a part in the increase of current due to hydrogen. The decrease cannot be ascribed to the formation of heavy negative ions[1] which tend to decrease the current because the current remains fairly well saturated. Heavy ions would not decrease the final current but would make saturation more difficult. The tests are in accordance with the tests made by others as previously mentioned.

The Effects of Hydrogen on the Current. Tests Nos. 4 to 8 Inc., 10 to 20 Inc.—A discussion of the effects of hydrogen is best made by considering the so-called "permanent effect" and the "temporary effect."

The permanent effect was first noted in Test No. 4. From Tests Nos. 6–7–8–10–11–12, the conclusion was drawn that the hydrogen itself does not produce a permanent effect. The permanent effect was due to something which was stopped by the refrigerant on the liquid air trap. Mercury vapor, grease vapor from the stopcocks and oil vapor from the pump were the only substances which could aid in producing the permanent effect. Mercury vapor alone and with hydrogen was found to give no permanent effect. The grease vapor was found to give a permanent effect. The oil vapor was not tested but in view of the results of a subsequent test with benzene, it is probable that it has the same effect as grease vapor. The grease and oil vapor slowly diffuse into the tube and when the filament is heated the vapor is decomposed giving the filament a coating of carbon which increases the current. Upon admitting air this coating is burned off and the current returns to its normal value. Hydrogen is not an essential to the permanent effect because the effect was obtained even with a good vacuum, but it hastens the action by carrying the vapor through the apparatus more rapidly.

The values of Richardson's constants given by the permanent effect and after heating the filament in grease vapor (in the same type of tube) are:

Permanent effect	$A = 10^8$,	$b = 54{,}000$.
Grease vapor	$A = 9.7 \times 10^8$,	$b = 58{,}400$.

These values are comparable and tend to further identify the permanent effect with the effect due to grease vapor.

[1] L. B. Loeb, PHYS. REV., 17, 89, Feb., 1921.

In a test not previously discussed, the filament was coated with a black deposit of carbon by heating in benzene vapor at about 1700° K. for several minutes. The values of Richardson's constants obtained in a vacuum with this carbon deposit were $A = 240{,}000$ and $b = 50{,}700$. These values are not so comparable with those given above, on account of the fact that another type of tube was used. Hydrogen at 0.27 mm. pressure was found to have no effect on the current from the carbon coated filament.

This permanent effect was found by Richardson [2] and later by Wilson [3] but was attributed to hydrogen dissolved in the platinum. The effect is described in the following excerpts from Dr. Wilson's book,[1] Chap. 3:

"In some experiments Richardson found that the leak from a hot platinum wire in hydrogen was independent of the pressure, even when this was reduced to a very small value. The writer found that this is always the case after a wire has been heated in hydrogen at a comparatively high pressure for some time. After this treatment the properties of a wire are completely changed."

"The wire then gives a large thermionic current practically independent of the pressure of the hydrogen from 760 mm. down to less than 0.001 mm."

"If the wire is heated in air or oxygen the large thermionic current immediately disappears. It can also be made to disappear by heating above 1700° C. in a very high vacuum. These facts make it very probable that the hydrogen combines with the wire, forming a very stable compound. This compound must have a very small dissociation pressure. It must also be formed very slowly unless the pressure of the hydrogen is high."

The characteristics of the permanent effect mentioned by Wilson are the same as those in the experiments of the writer. In view of the experiments described, the writer prefers to attribute the effect to grease or oil vapor rather than to hydrogen dissolved in the wire.

When hydrogen is admitted to a tube containing a new filament, there is a very large temporary increase in current and a slight permanent increase. In Test No. 19, the current was temporarily increased by a factor of 20 at 1800° K. with a gas pressure of only 0.078 mm. This increase falls off with continued heating and quite rapidly upon heating successively in air and hydrogen. The filament comes to a state in which the temporary effect is regular and can be reproduced provided the temperature is not raised too high. The increase in current due to the hydrogen is proportional to the pressure of the gas provided the pressure is above a certain minimum value.

With further heating in hydrogen and air at high temperatures, the temporary effect becomes smaller. In Test No. 20, the heating was continued until the effect had disappeared.

The conclusion is that the temporary increase in current when hydrogen is admitted is due to the action of the hydrogen not on platinum but on some impurity in the platinum. Alternate heating of the filament at high temperatures in air and hydrogen reduces the impurities to a state in which they cause no increase in current or frees the filament of them entirely. The latter action is the more likely. Carbon might be one of the impurities, but heating in air would take it from the filament. Then also, hydrogen was found to have no effect on the current from a deposit of carbon. An oxide of a metal, as calcium, for example, might be the impurity. It is known that hydrogen increases the current from calcium oxide. There is one thing to be pointed out: the action is not that of the reduction of an oxide to a metal, giving a larger emission, because as soon as the gas is removed the current returns to its normal value. In the case of the reduction of an oxide, oxygen would have to be present to bring the current back to its normal value.

The opinion had been that the temporary effect was due to hydrogen dissolved in the platinum. From this work it appears that the effect is due to hydrogen dissolved in the impurities in the filament but not in the platinum itself.

SUMMARY.

In closing, the writer wishes to express his sincere thanks to Dr. H. A. Wilson of Rice Institute, Houston, Texas, where this work was done, for his interest in the investigations and for his suggestions and criticisms which have led to the successful accomplishment of this work.

RICE INSTITUTE.

THE ELECTRON THEORY OF METALS IN THE LIGHT OF NEW EXPERIMENTAL DATA.

BY P. W. BRIDGMAN.

SYNOPSIS.

Deviations from Ohm's Law at High Current Densities of 5×10^6 amp./cm.^{2} have been detected in the case of Au and Ag foils, of the order of 1 per cent. Details will be reported elsewhere.

Effect of Mechanical Tension on Electrical Resistance.—For Li, Ca and Sb, as in the case of most metals, the resistance increases with the tension, whereas for Bi and Sr the coefficient is negative. Details will be reported elsewhere.

Modified Electron Theory of Electrical Conductivity has already been suggested by the author. It is assumed that the number of free electrons is relatively small; that their mean free path is many times the atomic diameter and depends on the amplitude of atomic vibration; and that the natural velocity of the electrons has the equipartition value. It is here *discussed in the light of the above new experimental data.* The deviations from Ohm's law support the theory since they require long mean free paths. For normal atoms for which the resistance decreases with increasing pressure, the electrons must pass directly from atom to atom through intervening atoms; but for the abnormal atoms Li, Ca and Sb, with both pressure and tension coefficients positive, the electrons seem to pass in channels between the atoms, somewhat as in Wien's theory. Diagrams are given showing the relation of the channels to the crystal structure. This simple conception enables the various coefficients of resistance to be connected quantitatively. The tension and temperature coefficients are calculated in terms of the pressure coefficients and the elastic constants and are found to agree approximately with the observed values.

Pressure Coefficient of the Wiedemann-Franz Ratio has been found to be negative for nine out of the eleven metals tested; that is, the thermal conductivity increases with pressure less rapidly than the electrical conductivity. Details will be reported elsewhere.

Elastic Wave Theory of the Atomic Part of Thermal Conduction in Metals.—The above result for the pressure coefficient means that an important part, probably at least one third, of the thermal conduction in these metals is performed by atoms, a conclusion confirmed by a comparison of Lorentz's theoretical value of the Wiedemann-Franz ratio with the experimental value. As a crude *picture of the atomic conduction*, it is suggested that the atoms are arranged in coherent strings separated from each other by gaps which each shift in position by the diameter of an atom each time the string on either side is hit, just like gaps between strings of billiard balls. Thermal energy is transferred when the gap shifts. By calculation, the maximum rate of propagation of a gap comes out about half the speed of sound in the metal, much less than the electronic velocity. The theory of electrical conduction already presented suggests that the length of the coherent strings of atoms is the same as the free path of the electrons, thus making possible a connection between the electronic and atomic contributions to thermal conductivity. If the number of atoms is of the order of 20 times the number of free electrons, as is to be expected from the above theory of electrical conductivity, then atomic conductivity comes out of the proper order of magnitude. A discussion of the temperature and

pressure coefficients of the atomic conductivity adds further evidence in favor of the probability of this theory. *Comparison with other theories.* It is similar to Debye's concept of thermal conduction in a crystal, but differs from Hall's ionization theory which, it is concluded, probably can account for only a small part of the conduction.

INTRODUCTION.

IN two papers in preceding numbers of this journal [1, 2] I have presented certain theoretical considerations with regard to the electron mechanism of electrical and thermal conduction in metals. Since writing these two papers, I have obtained three new sorts of experimental evidence bearing on the electron theory. In the first place, I have succeeded in detecting and measuring a departure from Ohm's law at high current densities in metallic gold and silver. In the second place, I have measured the effect of pressures to 12,000 kg./cm.^{2} on the thermal conductivity of eleven metals. And thirdly, I have measured the effect of mechanical tension on the resistance of those metals which are abnormal in that their resistance increases under hydrostatic pressure. It is the purpose of this paper to discuss the bearing of these new data on the electron theory of conduction as I have previously given it.

The theory which I have presented is a free path theory. It differs from the classical theory, which is also a free path theory, in the following respects: the number of free electrons is supposed small compared with the number of atoms, so that the free path is long compared with the distance between atomic centers, and the variations of resistance under changes of temperature or pressure are computed in terms of the variation of free path, which may be found from the variation of amplitude of atomic vibration, and in terms of the natural velocity of the electrons, for which the equipartition value is assumed, as in the classical theory. The evidence for the equipartition velocity is twofold: it is required to account for the universal value of the Wiedemann-Franz ratio, and it is also required to account for the universal value of the temperature coefficient of resistance.

The evidence seemed to be that there are two essentially different types of mechanism by which electrons pass through a metal. By far the most usual type is that of those metals whose resistance decreases with increasing pressure. In these metals it is probable that the electrons pass directly from atom to atom through the substance of the atom itself. There are a few metals, however, whose resistance increases under pressure. There are two possibilities in the way of mechanism for these abnormal metals. In the first place, the mechanism may be like that

[1] P. W. Bridgman, PHYS. REV., 9, 269–289, 1917.
[2] P. W. Bridgman, PHYS. REV., 17, 163–194, 1921.

above in that the electrons pass from atom to atom through the substance of the atom, but the law of force between atoms may be abnormal so that there are abnormalities in the way in which the amplitude changes with pressure (bismuth type), or the electrons may pass between the atoms in natural channels, much after the manner of the theory of Wien [3] (lithium type).

The Evidence from Ohm's Law.—The data are to be presented in detail in another place. The experimental fact is that the resistance of gold and silver in the shape of thin leaf has been found to increase by something of the order of one or two per cent. at current densities of the order of 5×10^9 amp./cm^2. Now J. J. Thomson [4] showed long ago on the basis of the classical theory that the resistance would be expected to increase at very high current densities, because the velocity of drift imparted to the electrons by the external field would no longer be small compared with the natural velocity of the electrons. It is evident that the velocity of drift imparted by the external field will be greater the longer the free path, that is, the longer the time in which the field has a chance to act on the electron without interference. On the basis of the length of free path assumed by the classical theory, which is equal to or less than the distance between atomic centers, the departures from Ohm's law would not begin to play an important rôle at currents below 10^{11} amp./cm^2. Since I am also assuming a free path mechanism, the fact that I find departures from Ohm's law at densities so much lower than predicted by the classical theory must mean that the free paths are much longer than the distance between atomic centers. Now this is exactly the kind of free path that other kinds of evidence have already made seem probable to me, so that this new experimental fact affords confirmation of the theory.

It is unfortunate that I can see no way of calculating exactly what the free path is in terms of the departures from Ohm's law. Such a computation involves a knowledge of the small departures from Maxwell's distribution law for the electrons at high fields, and this again I believe involves a detailed knowledge of the whole atomic structure. I am compelled therefore at present to leave this new experimental evidence with the bare statement that it makes exceedingly probable a long free path, and is in so far in accord with my theory.

Effect of Pressure on Thermal Conductivity.—The data for eleven metals are to be published in another place, to which reference must be made for the details. Only normal metals, whose electrical resistance decreases

[3] W. Wien, Columbia Lectures, 1913, 29–48.

[4] J. J. Thomson, The Corpuscular Theory of Matter, 1907, p. 55.

under pressure, were measured. The broad facts are that the thermal conductivity may either increase or decrease under pressure. For only two metals was the increase of thermal conductivity greater than the increase of electrical conductivity; for these two metals (lead and tin) the Wiedemann-Franz ratio increases under pressure, for the other metals it decreases.

In my theory I took over without essential modification the classical picture of thermal conduction as performed by the same electrons that carry the current. The reason for this was that I could see no other way of accounting for the approximate constancy of the Wiedemann-Franz ratio for different metals, and this seemed to me the one most striking and outstanding fact with regard to thermal conduction. So far as the conduction of electrical current and heat is by the same mechanism, one may expect the effect of pressure on the electrical and thermal conductivity to be the same, and hence the pressure coefficient of the Wiedemann-Franz ratio to be zero. The new experimental evidence requires therefore a reconstruction of our previous picture of the mechanism of thermal conduction. The modification is not very serious, however, and does not require us to abandon anything of our previous position. It has of course always been known that the picture of thermal conduction offered by the classical theory is not complete in that it neglects the part of the heat carried by the atoms. We now have to inquire what the probable magnitude of this neglected part of the thermal conductivity is, and whether it is not capable of explaining the new facts.

With regard to the probable magnitude of the atomic part of thermal conduction, it is well known that the original value of the Wiedemann-Franz ratio deduced by Drude from elementary considerations agrees with the experimental facts much better than the more rigorous value deduced by Lorentz,[5] Bohr,[6] and others. Lorentz's value is only two thirds that of Drude, and Drude's is slightly less than the experimental value. If we accept Lorentz's value as the one properly to be deduced from the theory, and his work has been abundantly checked by others, this would mean that the atomic part of the electrical conductivity may be at least half as large as the electronic part. This is a fairly large part to have at our disposal.

Now the electronic part of the thermal conductivity must increase under pressure at the same rate as the electrical conductivity. But the atomic part may conceivably either increase or decrease, and so the pressure coefficient may be either positive or negative. The only absolute requirement here is that the total decrease of conductivity under

[5] H. A. Lorentz, The Theory of Electrons, p. 65.

[6] N. Bohr, Studier over metallernes Elektrontheori, Copenhagen, 1911.

pressure must never be so great as to more than use up the initial atomic contribution, because the atomic contribution must always remain positive. In the experimental paper this question is examined in detail, and I have shown that there is never any trouble on this score.

We now have to consider more in detail what the nature of the atomic part (more specifically, the part not determined by the classical electron free path mechanism) of the thermal conductivity may be, and what may be expected as to the sign of its pressure coefficient. The following picture seems to satisfy the requirements as far as order of magnitude goes, and has the advantage of using part of the same mechanism that we have invoked to explain electrical conductivity. In the normal metal I have thought of the electron as passing through the substance of the atom, with a free path a good many atomic diameters long. A crude picture of this state of affairs is that the atoms in a metal are separated into many coherent strings, one string separated from the next by a distance greater than the normal, that is, by a "gap." These strings are in a constant state of flux, as the position of the gaps is continually changing. The length of the string is the free path of the electrons for electrical conduction. The mechanism by which the gap wanders about in the metal is an elastic mechanism; we imagine the head of the string being struck by the rear atom of the string ahead of it; the impacting atom sticks to the string, an impulse travels along the string, and the rear atom flies off, exactly as when a row of billiard balls in contact is struck by a single ball head on. Under the most favorable conditions the gap cannot travel ahead by more than the diameter of an atom during the natural period of atomic vibration. Now the natural period is known for a number of metals, and a numerical calculation shows that for all metals this maximum velocity of propagation of the gap is about one half the velocity of sound. This is much less than the velocity of free flight of the electrons. At 0° C. this latter is about 1.7×10^7 cm./sec., and the maximum velocity of sound for any metal is about 5×10^5. This means that for the electrons the gaps are practically stationary, so that our former picture of conduction is not at all affected by the motion of the gaps.

Now the mechanism of translation of the gaps, that is, the sticking of an atom to the head of the string and the flying off of one from the rear, is evidently one that is capable of conducting heat, if there is a temperature gradient in the metal. Precisely the same analysis may be applied to this case as to the ordinary kinetic problem of heat transfer. The important feature is that the free path for heat transfer is the same as the free path for electrical conduction. In my theory of conduction I

have assumed that there is equipartition of energy between the atoms and electrons. Let us call $f(\theta)$ the energy of either atom or electron as a function of temperature. Then for the part of the thermal conductivity due to the atoms, the ordinary transport analysis will give the formula

$$\mu_a = nl \frac{df}{d\theta},$$

and for the part due to the electrons the same analysis will give

$$\mu_e = \frac{1}{3} N_e v_e l \frac{df}{d\theta}.$$

Here N_e is the total number of free electrons (that is, electrons which take part in the conduction process) per cm.^{3}, v_e is the velocity of the electrons, l is the free path, and n is the number of atomic transfers of energy per second across unit section. Of these quantities n is the only one requiring further discussion. Its exact value will depend to a high degree on the structure of the crystal and the perfection of the fit between neighboring atoms, but we can at least set an upper limit. The maximum number of transfers of energy down each string of atoms is evidently the frequency of atomic vibration, ν, for this is the maximum number of collisions of the head of the string with the rear of the next. The number of strings crossing unit section is the number of atoms in unit section, or $N_a^{2/3}$, where N_a is the number of atoms per cm^3. Hence an upper limit for n is $\nu N_a^{2/3}$. If now we substitute this upper limit for n in the formula for μ_a, and take the ratio of the atomic to the electronic conductivity, we get

$$\frac{\mu_a}{\mu_e} = \frac{N_a}{N_e}\left(\frac{3\nu}{v_e N_a^{1/3}}\right).$$

The reasonableness of this may be checked as far as order of magnitude goes as follows. In the first place, μ_a/μ_e must be in the neighborhood of 0.5, for the actual Wiedemann-Franz ratio is usually about 50 per cent. greater than Lorentz's theoretical value. In the second place, my theory of electrical conduction demands that N_a/N_e be large, perhaps of the order of 100 or 1,000. If the velocity of migration of the gaps through the metal is the maximum, then N_a/N_e given by the above formula must also be of the same order, but since the migration velocity may well be much below the maximum, we may expect N_a/N_e to be smaller than the above, but still materially larger than unity. I have made the calculation in this way, putting $\mu_a/\mu_e = 0.5$, for the metals Al, Cu, Zn, Ag, and Pb. Nernst [7] gives the value of the frequency of these, and the other

[7] W. Nernst, Wolfskehlstiftung Vorträge, Göttingen, 1914, p. 77.

constants are well known. I find the following values respectively for N_a/N_e; 10, 15, 15, 15, 30. The order of magnitude of these is hence about what would be expected.

Another check as to the probability of this point of view is afforded by the variation of thermal conductivity with temperature. My theory of electrical conductivity gives a variation of electrical resistance as the absolute temperature, which of course agrees very approximately with the facts. Now theoretically the Wiedemann-Franz ratio is proportional to the absolute temperature; this means that that part of the thermal conductivity due to the electrons is independent of the temperature. This enables us to find at once the temperature coefficient of the atomic part of the thermal conduction. To find this, differentiate μ_e logarithmically, obtaining

$$\frac{1}{\mu_e}\frac{d\mu_e}{d\theta} = \frac{1}{N_e}\frac{dN_e}{d\theta} + \frac{1}{v_e}\frac{dv_e}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right).$$

We suppose, as always, that N_e is constant, and since $d\mu_e/d\theta$ is to be zero, this gives

$$\frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right) = -\frac{1}{v_e}\frac{dv_e}{d\theta} = -\frac{1}{2\theta},$$

since v_e^2 is proportional to θ. Now differentiate μ_a logarithmically, obtaining

$$\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} = \frac{1}{n}\frac{dn}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right)$$
$$= \frac{1}{n}\frac{dn}{d\theta} - \frac{1}{2\theta}.$$

Now assuming that n is a fixed fraction of its maximum value, the variation of n with temperature is small, since that of its factors N_a and ν is small, and may be neglected. (I have previously discussed the variation of ν with temperature.) [8] Hence finally,

$$\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} = -\frac{1}{2\theta}.$$

If now we attempt to allow for a change with temperature of the fractional part of its maximum value which n assumes, the probability seems to me that this fractional part will increase with rising temperature, since the change in amplitude of atomic vibration with rising temperature is large compared with the change in the distance of separation of atomic centers. This would mean that the temperature coefficient of the atomic part of thermal conductivity is more nearly positive than $-1/2\theta$.

[8] Reference 1, equation (4), p. 271.

We have now found that the atomic part of the thermal conductivity decreases with rising temperature. The other part remains constant, and hence we would expect the temperature coefficient of thermal conductivity of all metals to be negative, and to be largest numerically in those metals in which the atomic share in conductivity is largest. Now a large Wiedemann-Franz ratio means a larger proportional atomic conductivity. Hence if we plot Wiedemann-Franz ratio against temperature coefficient of thermal conductivity, we would expect the high values of the one to go with the high values of the other. I have plotted these values in Fig. 1 for most of the metals of this paper. It is known

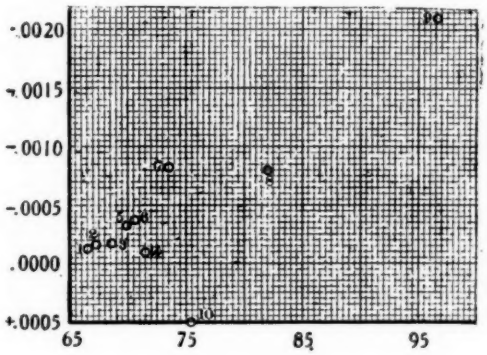


Fig. 1.

Temperature coefficient of thermal conductivity (ordinates) against Wiedemann-Franz ratio times 10^{-9} (abscissae). The metals shown are as follows: 1 Cu, 2 Zn, 3 Ag, 4 Pb, 5 Ni, 6 Cd, 7 Sn, 8 Fe, 9 Bi, 10 Pt.

that the temperature coefficient is extremely subject to experimental error, and different observers do not always agree. I have used the data of Jaeger and Diesselhorst,[9] by far the best, who made all the different sorts of measurements on the same samples of metal. Only for nickel do Jaeger and Diesselhorst not give the coefficient, and I have taken the temperature coefficient of conductivity from another observer.[10] All the metals of my pressure study are here included except antimony. With the exception of platinum, whose temperature coefficient of thermal conductivity is + 0.0005, and hence is entirely out of the class of the other metals, the correlation is strong between Wiedemann-Franz ratio and temperature coefficient, and hence lends probability to our view. With regard to platinum it may be said that its electrical resistance also behaves abnormally with regard to temperature, since it is one of a very few metals for which the curve of resistance against temperature is concave toward the temperature axis.

[9] W. Jaeger und H. Diesselhorst, Phys. Tech. Reichsanstalt, Wiss. Abh. 3, 269–425, 1900.
[10] M. F. Angell, PHYS. REV., 33, 421–432, 1911.

This point of view imposes a limit on the possible temperature coefficient of thermal conductivity. This must not be so high that the coefficient of the atomic part alone gets numerically greater than $-1/2\theta$, or about -0.0018. This is true for all the metals above except bismuth, which of course is abnormal in other respects. The restriction is most exacting in the case of tin, but is still met with a few per cent. margin of safety.

So much for the inherent probability of our picture of the part of thermal conductivity done by the atoms. Now with regard to the effect of pressure on this part of the conductivity, we may recognize two opposing tendencies.

Differentiate μ_a and μ_e logarithmically at constant temperature, obtaining

$$\frac{1}{\mu_a}\left(\frac{\partial \mu_a}{\partial p}\right)_\theta = \frac{1}{n}\left(\frac{\partial n}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{df}{d\theta}\right)$$

and

$$\frac{1}{\mu_e}\left(\frac{\partial \mu_e}{\partial p}\right)_\theta = \frac{1}{N_e}\left(\frac{\partial N_e}{\partial p}\right)_\theta + \frac{1}{v_e}\left(\frac{\partial v_e}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{dt}{d\theta}\right).$$

We suppose that N_e remains constant, and our assumption with regard to equipartition also means that v_e is constant at constant temperature. Hence $(1/\mu_a)\ (\partial\mu_a/\partial p)_\theta$ differs from $(1/\mu_e)\ (\partial\mu_e/\partial p)_\theta$ only by the term $(1/n)\ (\partial n/\partial p)_\theta$. Now in general we may put $n = \beta\nu N_a^{2/3}$, where β is a factor which at the maximum can reach only unity. The variations of N_a with pressure are comparatively unimportant, so that if β does not change, the proportional change of n is determined by the proportional change of ν. This has been computed in a previous paper.[11] It is the negative of the proportional change of amplitude, which in turn is approximately one half the pressure coefficient of resistance. ν therefore increases under pressure, and at such a rate as to contribute to the atomic part of the conductivity an increase about one half as rapid as the increase of electrical conductivity. The other factor, β, however, is the one that is likely to be important. Our previous discussion of the order of magnitude of N_a/N_e shows that β is probably much below its maximum value of 1, so that there is plenty of room for variations in either direction. I do not believe that we can predict its precise manner of variation until we know a great deal about atomic structure and the arrangement of the atoms in the crystal. The factor β is a measure of the frequency with which energy is handed on from one string of atoms to the next, and it is also a measure of the speed of migration of the gaps through the metal. Now a gap is a joint or fissure in the atomic structure due to

[11] Reference 1, equation (5), p. 271.

temperature agitation. Its permanence, or its ease of migration, will obviously depend on the details of the structure. It seems quite plausible to me that the speed of migration or mobility might either increase or decrease under pressure, with the probability that in most cases it will decrease, because with increasing pressure a group of atoms must find it more difficult to escape from their lack of fit by handing it on to the neighbors. An escape from lack of fit would seem to involve a local and temporary increase of volume, which is against the urge of the external pressure. The mobility of the gaps may involve something analogous to the internal viscosity of the metal. This has never been measured under pressure, but it is known that the viscosity of liquids increases greatly with pressure, and that the increase is proportionally greater for those substances with a high absolute value of viscosity, so that it is not unreasonable to expect a comparatively large pressure effect on the internal viscosity of metals.

As a matter of fact, it does turn out in the majority of cases that the increase of thermal conductivity is smaller than the electrical conductivity, or else is negative, so that the atomic part of thermal conductivity in many cases must decrease. In the case of lead and tin only is the increase of thermal conductivity so large as to indicate that for them β may increase with pressure.

This picture of the atomic part of thermal conduction is in many respects like Debye's[12] concept of thermal conduction in a crystal. He has heat conducted by elastic waves, which are dissipated by the lack of perfect homogeneity of the material. The waves have an equivalent "free path" defined in terms of the distance between inhomogeneities. He finds the cause of the inhomogeneities in local chance variations from the mean density, which he calculates by the thermodynamic formulas for "Schwankungen." His local inhomogeneities evidently function as my gaps, and in fact may be the same thing physically. Debye did not discuss metallic conduction. My assumption that the free path of the elastic waves is the same as that of the electrons seems a most natural one, but so far as I know, has not been employed before. Notice in this connection that the purely atomic part of the conductivity in a metal is large compared with the total conductivity of such crystals as rock salt.

There are other possible factors to be taken into account. In the first place, the free path is not actually so cleanly defined a thing as we have supposed above. As the electrons pass from atom to atom they are subject to a certain amount of interference at every passage; there

[12] P. Debye, Wolfskehlstiftung Vorträge, Göttingen, 1914, 43–60.

is no catastrophic change every now and then as we have supposed, and the free path idea can only be a rough description of an average state of affairs. The same sort of thing must of course be recognized in applying kinetic theory to condensed gases or liquids. Kleeman has emphasized in his recent book[13] this indefinite character of the concept of a free path, and has shown that a great many kinds of free path must be recognized. For any particular sort of phenomenon, mean free path is defined in a corresponding particular way. The free path for viscosity, for example, is defined in terms of velocity transfer, and for heat conduction in terms of energy transfer. Kleeman has shown that different sorts of free path may differ in rare cases by factors of as much as 10. We would expect to find the same sort of thing in a metal, so that the free path of electrical conductivity (which is concerned with a velocity transfer) would not be the same as the free path of thermal conductivity (which is concerned with a kinetic energy transfer). This may account partly for the difference between the observed and computed Wiedemann-Franz ratio. It is also possibly conceivable that the two different kinds of path should be differently affected by pressure, so that the pressure coefficients might have opposite signs. The theory is not far enough advanced, however, to allow us to make any quantitative use of it. All that has hitherto been done is to calculate back from the experimental data to show that there must be different kinds of path if the kinetic formulas are correct. We cannot yet solve the direct problem of predicting in terms of the atomic structure what the relation between the different sorts of path will be, and it is the direct problem that must be solved for the present purpose.

There is a second possibility that I have considered. Professor Hall[14] has a theory of thermal conduction in terms of the heat of ionization of the atoms. This sort of a mechanism seems at first sight exactly what we need to explain the pressure coefficient of thermal conduction, because it is natural to suppose that the heat of ionization becomes less as the pressure becomes greater, and for this reason the thermal conductivity would decrease with rising pressure. But there is another factor to consider, namely, the number of ions per cm^3. If this number is connected with the heat of dissociation by the ordinary formula $n = n_0 e^{-(w/K\theta)}$, a decrease in the heat of ionization will be accompanied by an increase in the number of ions, so that for this reason the thermal conductivity will increase. A numerical discussion with probable values, for instance assuming such a heat of ionization that the atoms are 1/1,000 ionized, shows that the increase of numbers far overbalances the decrease of

[12] R. D. Kleeman, A Kinetic Theory of Gases and Liquids, Wiley and Sons, 1920.

[14] E. H. Hall, PHYS. REV., 11, 329, 1918.

heat of ionization, so that on the whole the conductivity will increase under pressure, instead of decrease. Another objection to Professor Hall's theory is that it gives no account of the Wiedemann-Franz ratio. Of course a mechanism like that of Professor Hall's theory must be present in the metal, simply because the presence of free electrons involves the presence of ions, but my own feeling is that this part of thermal conduction is not so important as some others.

Effect of Tension on the Resistance of the Abnormal Metals.—The experimental results are published at length in another place. Briefly, the essential facts are these. There are five metals known to be abnormal in that their resistance increases under pressure, Bi, Sb, Li, Ca, and Sr. Of these only two, Bi and Sr, are abnormal also with respect to the effect of tension, in that their resistance decreases under tension. The resistance of Li, Ca, and Sb increases under tension, as is normal. In the detailed paper I have shown that the metals with a "Bismuth mechanism" would be expected to act as Bi does under both tension and pressure, and that metals of the "Lithium mechanism" would be expected to act like Sb, Li, and Ca under tension and pressure. Considerations were given that made it likely that both sorts of mechanism were involved in Sr.

It is my purpose here to consider further the three metals Li, Ca, and Sb. The account which I have previously given of the effect of pressure and temperature does not apply to metals of this type. Further, the three metals are of particular interest in the apparently great simplicity of their mechanisms. This simplicity makes possible a deduction of expressions for the temperature and tension coefficients of resistance in terms of the pressure coefficient and other unrelated data.

In metals of the lithium type, the electrons are to be thought of as travelling in channels between the atoms. Under external changes, the channels change in dimensions, both because the centers of the atoms are changed in position and because the amplitude of atomic vibration is changed. For those changes which take place at constant temperature our problem is to deduce the changes of resistance in terms only of the changes in cross section of the channels; if the temperature changes also, the change of resistance involves both the change of dimensions of the channels and the changes of velocity of the electrons with temperature.

The details of the computation will involve a knowledge of the crystalline structure and the relation of the channels to that structure. The structure of lithium is known to be space centered cubic;[15] the structure of

[15] A. W. Hull, PHYS. REV., 10, 689, 1917.

calcium is face centered cubic;[16] the structure of antimony is complicated,[17] consisting of two interpenetrating lattices, but it is very approximately simple cubic in structure, and for our purposes it will be good enough to treat it as simple cubic.

In Fig. 2 is shown a view of spheres piled in space centered cubic

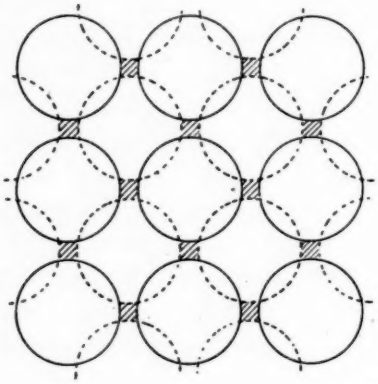


Fig. 2.

One view of spheres in contact in space centered cubic arrangement. The shaded areas indicate open channels.

arrangement, the diameters of the spheres being such that they are in contact with each other. The dotted circles show the spheres in the layer below the full spheres. The diagram shows that there are open channels between the spheres through which the electrons may pass. Of course if the atoms are not large enough to be in mutual contact, the channels are even larger.

In Fig. 3 is shown one view of spheres in mutual contact in face centered

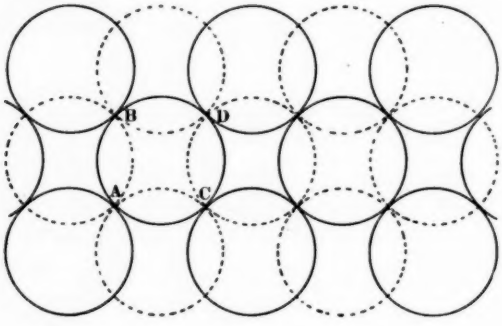


Fig. 3.

One view of spheres in contact in face centered cubic arrangement. Channels open where shown by the letters if the distance between atomic centers is slightly increased.

[16] A. W. Hull, PHYS. REV., 17, 42–44, 1921.

[17] R. W. James and N. Tunstall, Phil. Mag., 40, 233–239, 1920.

cubic arrangement. Now in this structure there are no open straight channels, but if the centers of the spheres are held fast, while their radii decrease, channels open in the locations indicated by the letters, and the plane section of the crystal becomes similar to that of the space centered crystal of Fig. 2. In fact Fig. 3 goes into Fig. 2 on rotation through 45°. (The distance of separation of the planes of the full and the dotted spheres does not become the same for the two kinds of crystal, however.) Now the crystallographic evidence proves that in the crystal of metallic calcium the atoms cannot be in contact,[18] and hence we assume the channels in metallic calcium to be in the place shown.

If the structure is simple cubic with the spheres in contact, the spaces between the full circles of Fig. 2 show the location of the channels. It seems more likely, however, that the atoms of Sb are not spherical, but are more nearly cubic, filling the space more completely. One reason why this seems probable is that spheres in simple cubic piling are exceedingly unstable, whereas cubes in simple cubic piling are as stable as possible. Fig. 4 therefore probably represents a closer approach to the

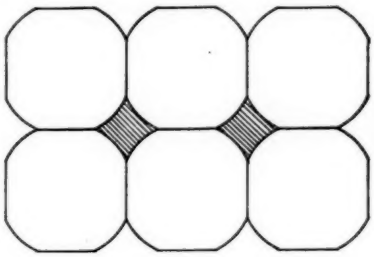


Fig. 4.

One view of approximately cubic atoms in simple cubic piling. The shaded regions show open channels.

case for antimony, the atoms having the shape of rounded cubes, and the channels being in the grooves between the edges, as shown.

We have now to consider the effect of temperature agitation on the size of the channels. The atom is to be thought of as of a fixed size, but at higher temperatures it occupies an effectively larger space in virtue of its temperature agitation. Under these conditions the section of the channel for all three types of crystal structure may be represented approximately as in Fig. 5. The full circles show the outlines of the stationary atoms, and the dotted circles the space effectively occupied by them in virtue of temperature agitation. If we call "a" the radius of the atom, α its amplitude of temperature vibration, c the width of the

[18] Reference 16, p. 44.

channel at the place shown, and L the distance between atomic centers in the direction indicated, then

$$L = 2a + 2\alpha + c.$$

Call δ the closest distance of approach of atomic centers. There is a relation between L and δ which is different for the different crystal systems.

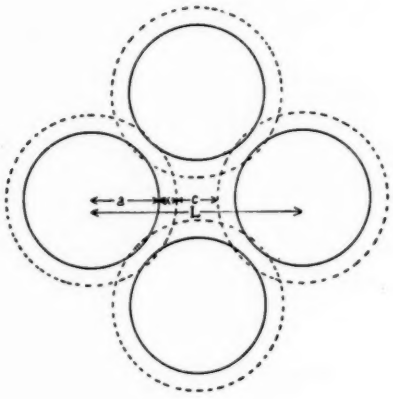


Fig. 5.

Shows the effective relations between the size of the atom, the space occupied by temperature agitation, and the open channels.

Simple cubic, $L = \sqrt{2}\delta$,
Face centered cubic, $L = \delta$,

Space centered cubic, $L = \frac{2}{\sqrt{3}}\delta$.

We now assume the free path of the electron, l, to be proportional to the section of the channel, which to a sufficient degree of approximation we may put equal to c^2. (The precise factor of proportionality between the area of the channel and c^2 does not enter the result so long only as it stays constant.) The resistance is inversely as l, and directly as v, the electronic velocity.

Our program calls in the first place for a computation of c in terms of the pressure coefficient of resistance, and then for a computation of the tension and temperature coefficients.

Denote the resistance by w. Then at constant temperature,

$$w = \frac{\text{const.}}{c^2},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial p}\right)_\theta,$$

whence

$$c = -\frac{2\left(\frac{\partial c}{\partial p}\right)_\theta}{\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta}.$$

$(1/w)\ (\partial w/\partial p)_\theta$ is known experimentally. To find $(\partial c/\partial p)_\theta$ we have

$$\left(\frac{\partial L}{\partial p}\right)_\theta = 2\left(\frac{\partial \alpha}{\partial p}\right)_\theta + \left(\frac{\partial c}{\partial p}\right)_\theta.$$

$(\partial L/\partial p)_\theta$ may be found as follows. Obviously

$$\frac{1}{L}\left(\frac{\partial L}{\partial p}\right)_\theta = \frac{1}{3}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\theta,$$

and the cubic compressibility is known. We now need the absolute value of L. The absolute value of δ may be found in terms of the atomic volume, V, and the mass of the hydrogen atom by the formula

$$\delta = \gamma(m_H V)^{1/3},$$

where γ is a factor depending on the crystal system.

Simple cubic, $\gamma = 1$,

Face centered cubic, $\gamma = (2)^{1/6} = 1.123$,

Space centered cubic, $\gamma = \frac{\sqrt{3}}{2^{2/3}} = 1.09$.

Using the above equations for L in terms of δ, we can now find the absolute value of L, and hence can compute $(\partial L/\partial p)_\theta$.

Our next problem is to compute $(\partial \alpha/\partial p)_\theta$. In a previous paper [19] I have shown that

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\theta = -\left(\frac{\partial v}{\partial \theta}\right)_p \Big/ C_p.$$

Hence we can find $(\partial \alpha/\partial p)_\theta$ if we can find α. To get α, we use the equipartition law. In a solid, the atom has six degrees of freedom, and therefore its maximum kinetic energy is twice the energy of a gas molecule at the same temperature. If the atom executes simple harmonic vibrations of frequency ν, at 300° Abs. we have

$$\frac{m}{2}4\pi^2\nu^2\alpha^2 = 2 \times 300 \times 2 \times 10^{-16}.$$

The problem of determining α is reduced to determining ν. The best way would be from the specific heats at low temperatures, but the data

[19] Reference 1, equation (6), p. 271.

do not seem to have been obtained. In default of a better, we may use Lindemann's formula in terms of melting temperature, atomic weight, and atomic volume

$$\nu = 3.08 \times 10^{-12} \sqrt{\frac{T_s}{m V^{2/3}}}.$$

We now have all the material to compute the required quantities, eventually getting c, and also a, the atomic radius.

Our next task is to compute the changes of resistance under tension. Our general picture is as follows. When the metal is stretched longitudinally it contracts transversely, the channels becoming constricted, and the resistance increases. Since the tension is applied at constant temperature, we have as before $w = \text{const.}/c^2$, and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta,$$

where T denotes tension. $(\partial c/\partial T)_\theta$ can be found from the equation $L = 2a + 2\alpha + c$, provided we can get $(\partial\alpha/\partial T)_\theta$, for $(\partial L/\partial T)_\theta$ may be obtained in terms of the elastic constants. In fact

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{\sigma}{E},$$

where σ is Poisson's ratio, and E is Young's modulus. With regard to the changes of α under tension, we do not know much. In the first place, the substance becomes anisotropic under tension, so that changes of α are different in different directions. It is probable, however, that the changes of α are not important, and we shall neglect them. This may be approximately justified as follows. Neglecting anisotropy, a thermodynamic discussion of the changes of the average α with tension may be carried through on the same basis as the preceding discussion for the changes of α with pressure.[20] In that analysis we should have to replace p by T, and v (volume) by l (length). We would find for the final result

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial T}\right)_\theta = -\left(\frac{\partial l}{\partial \theta}\right)_T \Big/ C_T.$$

Now C_T, specific heat at constant tension, is very nearly the same as C_p, and $(\partial l/\partial\theta)_T = \frac{1}{3}(\partial v/\partial\theta)_p$. Therefore the proportional change of α under 1 kg./cm.^{2} tension is approximately one third of its change under 1 kg./cm.^{2} pressure. But on the other hand, the changes of dimensions under 1 kg. tension are considerably larger than under 1 kg. pressure, so that

[20] Reference 1, p. 271.

it is probable that under tension changes of α are relatively much less important than under pressure. But an examination of the figures above will show that even under pressure the changes of α are not important compared with the changes of dimensions (L), and we shall therefore neglect $(\partial\alpha/\partial T)_\theta$.

Hence we have

$$\left(\frac{\partial c}{\partial T}\right)_\theta = \left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{L\sigma}{E},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = \frac{2}{c}\frac{L\sigma}{E}.$$

The tension coefficient is computed in this way and listed in the table. The computed value is 2/3 the observed value for Li, and 3/2 of it for Ca and Sb.

Finally we have to compute the temperature coefficient of resistance. According to our previous theory the changes of resistance with temperature depend on two factors; one of these is the change of the velocity of the electrons with temperature. This part of the change is $1/2\theta$, and is the same now as previously. The second part of the change of resistance is due to the change of free path. For normal metals I have shown that this change is also $1/2\theta$. The free path mechanism of these three abnormal metals is, however, entirely different from that of the normal metals, and the previous analysis fails. Our problem is to recompute the second part of the variation.

Now for changes of temperature, the conditions are the exact reverse for changes of tension. Here the changes of dimensions of the metal are unimportant compared with the changes of amplitude of atomic vibration. One may easily check this by a simple calculation. (I have already gone into the matter in connection with the pressure effects.) [21] In order to entirely get rid of the effect of changing dimensions, we will compute the temperature coefficient of resistance at constant volume instead of at constant pressure. The two coefficients differ by only a few per cent.; the exact formulas will be found in the place last cited.

For changes of resistance at constant volume we now have

$$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v = \frac{1}{2\theta} - \frac{2}{c}\left(\frac{\partial c}{\partial \theta}\right)_v.$$

To find $(\partial c/\partial\theta)_v$, we differentiate the equation $L = 2a + 2\alpha + c$, obtaining

$$\left(\frac{\partial c}{\partial \theta}\right)_v = -2\left(\frac{\partial \alpha}{\partial \theta}\right)_v.$$

[21] Reference 1, p. 272.

Metal.	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta$.	$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.	ν.	δ.	L.	$\left(\frac{\partial L}{\partial p}\right)_\theta$.	α.	$\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.
Li.....	6.8×10^{-6}	-10×10^{-6}	10.6×10^{12}	3.11×10^{-8}	3.60×10^{-8}	-10.8×10^{-14}	2.16×10^{-9}	-21.6×10^{-15}
Ca.....	10.6	− 7.7	5.4	3.94	3.94	− 7.5	1.77	− 13.7
Sb.....	12.2	− 2.26	3.23	3.18	4.46	− 3.57	1.71	− 3.86

	$\left(\frac{\partial c}{\partial p}\right)_\theta$.	c.	a.	$-\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta$.	$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta$.	$\frac{1}{\theta}\left(\frac{1}{2}+\frac{2\alpha}{c}\right)$	$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v$.
Li.....	-6.5×10^{-14}	1.91×10^{-8}	0.62×10^{-8}	3.2×10^{-5}	4.8×10^{-5}	.0027	.0043
Ca.....	− 4.8	0.905	1.34	1.24	0.84	.0033	.0030
Sb.....	− 2.80	0.459	1.83	0.73	0.50	.0046	.0049

But we have already found that

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\theta}\right)_v = \frac{1}{2\theta}.$$

Hence finally

$$\frac{1}{w}\left(\frac{\partial w}{\partial\theta}\right)_v = \frac{1}{\theta}\left(\frac{1}{2} + 2\frac{\alpha}{c}\right).$$

The results of computation by this formula are given in the table. The result is distinctly low for Li, but is as close to the experimental value as could be desired for Ca and Sb. The agreement would be expected to be closer for the temperature than for the tension coefficient, because there is here no assumption so questionable as our neglect of $(\partial\alpha/\partial T)_\theta$ in computing the tension coefficient.

Comment seems to be called for in one particular with regard to the values found for lithium. The calculated atomic radius is so small that the spheres of influence do not overlap, and the effective section of the channels is not in appearance like that shown in Fig. 5. I have therefore made a more exact computation for this case, putting as the fundamental equation

$$\text{Area of channel} = L^2 - 2\pi(a + \alpha)^2.$$

The analysis may be carried through on the exact lines of the above, except that instead of linear equations there are quadratics to solve. The result differs by only a few per cent. from that found by the simpler method, and it does not seem worth while to reproduce it. The essential feature in determining the result is the variation of the channel as c^2. It is also to be noticed that the values found for the radius of antimony justify our assumption of the rounded cube shape.

In connection with the small value of the effective radius of lithium as compared with the distance between atomic centers in the metal, it is interesting that Born[22] has recently arrived at a result of the same order of magnitude for the diameter of the lithium ion in solution. His value for the effective radius is 0.45×10^{-8} cm. against 0.62×10^{-8} cm. calculated above. Born states that the nature of his approximations is such that his result is small rather than large.

Our picture of the mechanism has been crude in the following particulars, among others. In the first place the assumption of the quantum theory of solids, which is at the basis of the formulas for the variations of α and ν, that the entropy is a function only of ν/θ, is probably not exact, and at any rate should have more careful verification. In the second place, Lindemann's formula for the frequency in terms of the melting

[22] M. Born, ZS. Elektrochemie, 26, 304, 1920.

temperature is known to be only an approximation for a number of substances. Thirdly, our assumption that the atoms act as if possessing a well-defined bounding surface of surface of definite shape can only be an approximation. In the case of lithium this approximation would seem to be particularly rough when one considers the atomic structure of lithium in terms of a nucleus and only three surrounding electrons. In fact, it is most difficult to see how the atom of lithium can have such a symmetry as to compel a crystal edifice of space centered cubic symmetry.

In view of the roughness of many of the assumptions it seems to me that the agreement of the observed with the computed values is as close as could be expected, and indicates that our picture of the mechanism is correct in the essential features. It is to be remembered that, so far as I know, there has been no previous attempt to account for the tension coefficient of resistance, and also that there has been no account given of the departure of the temperature coefficient from exact equality with $1/\theta$.

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A GRAPHICAL STUDY OF THE STABILITY RELATIONS OF ATOM NUCLEI.

BY WILLIAM D. HARKINS AND S. L. MADORSKY.

SYNOPSIS.

Graphical Study of the Electrical Properties of Atomic Nuclei and their Relation to Stability.—The properties considered are: P the number of positive electrons in the nucleus, which is taken to be numerically equal to the atomic weight, M the net positive charge which is equal to the atomic number, N the number of negative electrons which is equal to $(P - M)$, $[(N/P) - \frac{1}{2}]$ the excess of the relative negativeness N/P over the minimum $\frac{1}{2}$, and n the isotopic number which is equal to $(P - 2M)$ and also to $(N - M)$. The relations between each of these five quantities and each of the others for the various atomic nuclei are shown in ten two-dimensional plots which clearly bring out the stability relations and are of particular interest because of the limited region in each plot where atoms are found. Except in the case of hydrogen and of the helium isotope $P = 3$, N/P is never less than $\frac{1}{2}$ and M/P is never greater than $\frac{1}{2}$; in fact for 85 per cent. of the atoms composing the crust of the earth, both these ratios are equal to $\frac{1}{2}$ and n is equal to zero. As the atomic number, that is the net positive charge increases, the *relative negativeness necessary to stability* increases above $\frac{1}{2}$, more and more; that is, as alpha particles are added extra cementing electrons are required to overcome the increasing mutual repulsion of the positive units of the nucleus. An alpha ray transformation does not change n but increases N/P, while a beta ray change decreases n by 2 units and also decreases N/P; we therefore find that in each group of isotopes, the ones with larger values of N/P show greater beta-ray and less alpha-ray instability. Stability considerations also help explain the fact that the *number of isotopes* is on the whole smaller for the lighter atoms. The curves bring out other interesting relations. The number of isotopes is larger for even than for odd numbered elements, especially for $M \leqq 30$. Also for most atoms, M, n and P are either all even or all odd, but N is usually even. The curve for the *frequency of occurrence of atoms* as a function of n shows periodic maxima four units apart, while as a function of M (or of N) the periodic maxima are two units apart. These regularities make it possible to predict the existence of the more abundant isotopes of elements whose mean atomic weights are accurately known; for instance, in the cases of lithium and boron predictions made in 1920 were later verified by Aston and by Dempster.

IN 1914 Rutherford [1] suggested that the hydrogen nucleus is the positive electron, and that the explanation of the fact that the helium atom has not quite four times the mass of the hydrogen atom, may be due to a "packing" effect. Less than a year later, Harkins and Wilson,[2] without knowing of this suggestion, published a careful study of the atomic weight relations of the elements, and developed what has since become known as the whole number rule, which is that pure atomic

[1] Rutherford, Phil. Mag., *27*, 494–5 (1914).

[2] Harkins and Wilson, Proc. Nat. Acad. Sci., *1*, 276 (1915); J. Am. Chem. Soc., *37*, 1367–1421 (1915).

species other than hydrogen, have atomic weights which are whole numbers, or very nearly whole numbers on the basis of oxygen as 16 or carbon as 12. This was stated in the form of an hypothesis: that the packing effect in the formation of helium from hydrogen amounts to about 0.77 per cent., but that the further packing which occurs in the formation of more complex atoms is so slight as to be obscured by the errors in the atomic weight determinations made on pure isotopes. The evidence of the chemically determined atomic weights of pure atomic species seems to justify the statement that while the atomic weight of free hydrogen is about 1.0078, the mean atomic weight of hydrogen in any complex atom is 1.000 ± 0.001.

Using these ideas as a basis, Harkins has developed a theory of nuclear stability and composition which indicates, among other important relations, that the elements fall into two classes which are on the whole essentially different in both stability and composition. These are: (1) Elements of even number, whose atoms are in general the more stable and the more abundant, and whose nuclei are mostly built up from alpha particles alone or of these together with negative electrons, whenever the nuclear system is not too complicated—that is when the atoms are light. Heavier atoms of this class have in general atomic weights which are divisible by two. (2) Elements of odd atomic number, whose atoms as a whole are less stable and less abundant, and contain in general three (sometimes one or two) hydrogen nuclei in addition to the alpha particles which constitute the greatest part of their composition. It was pointed out that the magnitude of the packing effect is likely to be different for the additional hydrogen nuclei from that found in the alpha particle. In general the atomic weights of pure atomic species of this class are odd numbers. The number of isotopes of elements of even atomic number is in general considerably larger than for elements of odd atomic number.

The atoms may be classified in a different way as (*A*) those of low atomic number (up to 28) which are in general by far the more abundant, and presumably the more stable. The number of isotopes for these elements is in general small. The atoms of elements (*B*) of high atomic number (heavy atoms) are rare, and presumably less stable than those of the light elements, but the number of isotopes (especially for the elements of even atomic number) is much higher.

If the nuclei of atoms are built up from positive and negative electrons, as indicated by the theory, it is easily seen that the number of particles involved is so great, for example 232 positive and 142 negative electrons, or 58 alpha particles, as to make the mathematical treatment of the

stability relations extremely difficult, especially since practically nothing is known concerning the laws of force or of the dimensions or form of the electrons in the nucleus. It seems worth while to make a simple beginning in this direction by plotting graphically the data now known which have a bearing upon the stability of atom nuclei, making use of such variables as seem to be related to this property.

Notation.

P atomic weight, or number of positive electrons.
M atomic number, or positive charge on nucleus.
N $P-M$, or number of negative electrons in the nucleus.
n Isotopic number.
p a positive electron.
e a negative electron.
a an alpha particle.
pe a neutron.

Variables Related to Atom Nuclei.

Two important variables related to the properties of the atom are the atomic weight (P) determined experimentally by chemical methods or by the use of positive rays, and the atomic number (M), which is also determined experimentally. This has been done by the use of the x-ray method of Moseley, and also by the independent method of noting the position of the element in the periodic system of Mendelejeff, which is simply a classification of the elements according to their properties as determined experimentally. The difference of two experimentally determined numbers (N) is also an experimentally determined number. In an exposition of the stability relations two additional dependent variables have been found to be of great convenience. These are the ratio N/P, which may be designated as the *relative negativeness* (presumably of the nucleus), and the isotopic number (n), which specifies the number of an isotope. The isotopic number may be defined as equal to $P - 2M$, so it may also be determined experimentally.

Since the mass and positive charge of an atom seem to be always associated, the term nucleus will be used to refer to that part of the atom which has these properties. The five variables listed above may be assumed to refer specifically to this part of the atom. As only two of the variables are independent, it is obvious that all of them may be represented on a single plane diagram, but, since in such a diagram only two of the axes are found to be at right angles to each other, it is necessary to use rectangular axes for each pair of variables if the relations which

[1] Obviously P/N may be used as the relative positiveness.

exist are to be made sufficiently obvious. In this way ten two-dimensional diagrams are obtained (Figs. 1 to 10).

Of the five variables under discussion only one, N/P, involves the ratio of two others. The other four give rise to six two-dimensional plots (Nos. 1, 2, 3, 8, 9, 10), each of which has the remarkable property that on it *constant values* of every one of the *five* variables, including N/P, are represented by *straight lines*. While this is obviously true of any set of whole number variables defined as these four are, independently of any atomic relationships, the importance of the diagrams consists in the fact that they give a good exposition of the elementary stability relations of complex nuclei. The characteristics of the ten two-dimensional plots are listed in Table I.

TABLE I.

Outline of the Ten Two-Dimensional Plots of the Variables P, M, N, n, and N/P, together with Equations representing Constant Values of the Variables.

(The ratio N/P is represented by R, and $(N/P) - 0.5$ by R'.)

Figure.	Independent Variables.	$R = k$, $R' = k'$.	$N = k$.	$P = k$.	$M = k$.	$n = k$.
1	P N	$N = PR$	$N = k$	$P = k$	$N = P - M$	$N = \frac{P+n}{2}$
2	M P	$P = \frac{2M}{1-2R'}$	$P = M + N$	$P = k$	$M = k$	$P = 2M + n$
3	M N	$N = \frac{M(1+2R')}{1-2R'}$	$N = k$	$N = P - M$	$M = k$	$N = M + n$
4	M R'	$R' = k'$	$R' = \frac{N-M}{2(N+M)}$	$R' = \frac{P+2M}{2P}$	$M = k$	$R' = \frac{n}{2(n+2M)}$
5	P R'	$R' = k'$	$R' = \frac{2N-P}{2P}$	$P = k$	$R' = \frac{P-2M}{2P}$	$R' = \frac{n}{2P}$
6	N R'	$R' = k'$	$N = k$	$R' = \frac{N}{P} - 0.5$	$R' = \frac{N-M}{2(N+M)}$	$R' = \frac{n}{2(2N-n)}$
7	n R'	$R' = k'$	$R' = \frac{n}{2(2N-n)}$	$R' = \frac{n}{2P}$	$R' = \frac{n}{2(2M+n)}$	$n = k$
8	M n	$n = \frac{4R'M}{1-2R'}$	$n = N - M$	$n = P - 2M$	$M = k$	$n = k$
9	P n	$n = 2PR'$	$n = 2N - P$	$P = k$	$n = P - 2M$	$n = k$
10	N n	$n = \frac{4R'N}{1+2R'}$	$N = k$	$n = 2N - P$	$n = N - M$	$n = k$

Note.—All of the fifty lines for constant values in the ten figures are straight except eight, as can be seen from the equations.

It should be noted that the position of the actinium series in these ten plots is in accord with the relations of this series as they have been given by Soddy; the actual relations being undetermined as yet. According to E. Q. Adams the atomic weight of actinium is an odd number, and that lead from actinium has an atomic weight of 207. This would fit in with the general system fully as well or even better than the scheme proposed by Soddy. Adams' system would be represented if each symbol for an element of this series were to be raised by *one isotopic* number, the atomic number being kept the same.

1. *P*, *N* PLOT, AND THE ISOTOPIC NUMBER.

The remarkable feature of the plot which represents the number of negative electrons on the Y axis, and the number of positive electrons on the X axis is shown by the line with a slope of 1/2 which extends to the right from the origin. In no case is the point which represents the position of any species of complex atoms below this line, though hydrogen, and Rutherford's helium isotope of mass 3 lie below it. However the former of these two is simple, and the latter has not been found to exist as an atomic species. It is of extraordinary interest that 85 per cent. of all of the atoms in the surface of the earth, and 79 per cent. of the atoms in the meteorites are represented by points which lie exactly on this line, on which the relative negativeness to positiveness of the atom nuclei is just as 1 to 2, or 1/2. Since the formula of any nucleus of this type is $(p_2e)_M$, or $a/2$ it has been suggested by Harkins that the group p_2e may be the most fundamental group concerned in atom building. However, since for more than 99.9 per cent. of the atoms of this formula M is an even number, it seems that, if this group exists, it is very unstable with respect to aggregation, and unites with itself to form groups of the formula $(p_2e)_2$, which are alpha particles.

All of the pure atomic species which are represented by points which lie above this line, lie on 54 lines parallel to it; whose slope is therefore also 1/2. These are lines of constant isotopic number. The isotopic number of the line of this slope which passes through the origin is zero, the isotopic number of ordinary uranium is 54. The space available for these lines in the diagram is so small that only the zero line is represented. On this plot the lines of constant atomic number have a slope of 1 to 1, or along such lines N must increase by 1 if P increases by 1, so the formulæ of isotopic nuclei differ by one or more neutrons of the formula pe. Thus the nucleus of any atom is represented by the formula $(p_2e)_M\,(pe)_n$, where n is the *isotopic number*. The chart of the radioactive elements shows, as is evident from the formula of the alpha particle

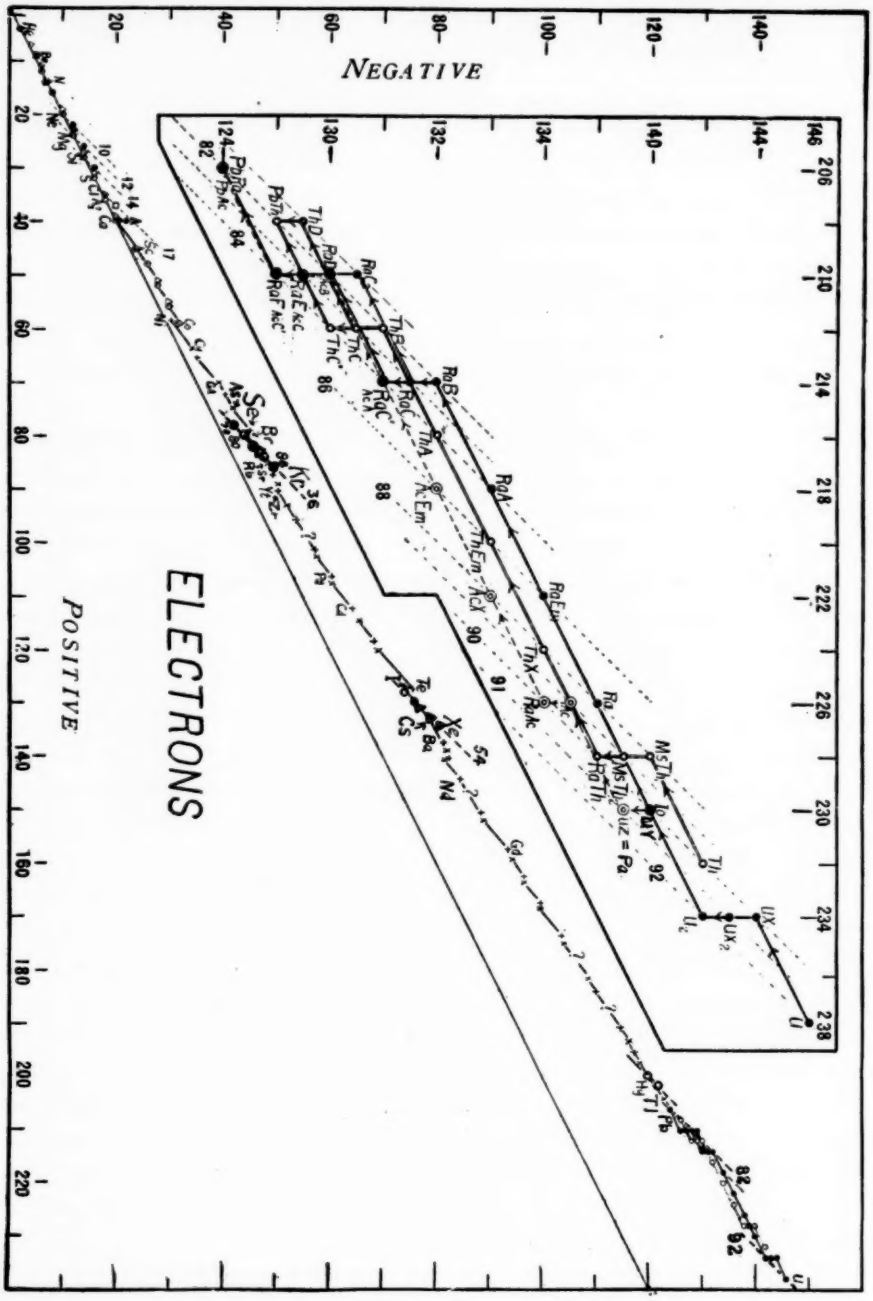

Fig. 1.

Plot of the total number of negative and positive electrons in atom nuclei. Isotopes ($P - N$ = a const.) lie on lines (dotted when they are given) which have a slope of 45°. Members of the helium-thorium series are represented by open circles, of the metaneon-uranium series by circles which are inked in, the lithium series by triangles, and metachlorine (37) by a square. Note that the elements of the helium-thorium series from helium to calcium, and the radioactive elements in any series during successive alpha disintegrations, lie on lines which have a slope exactly equal to 0.5.

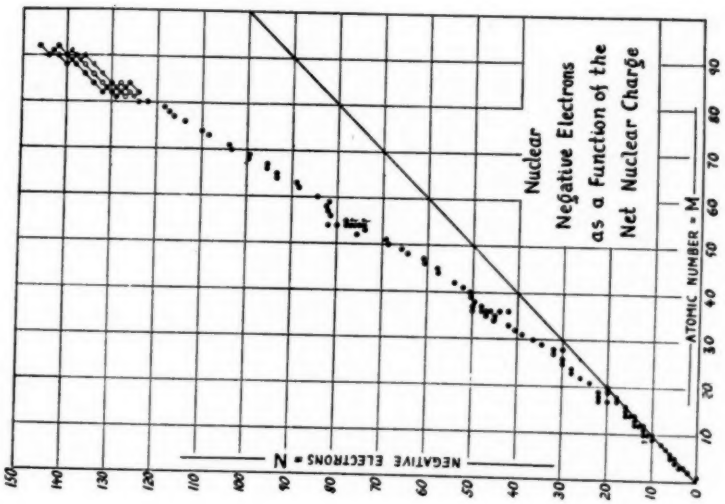
Nuclear
Negative Electrons
as a Function of the
Net Nuclear Charge
NEGATIVE ELECTRONS = N
ATOMIC NUMBER = M

Fig. 3.

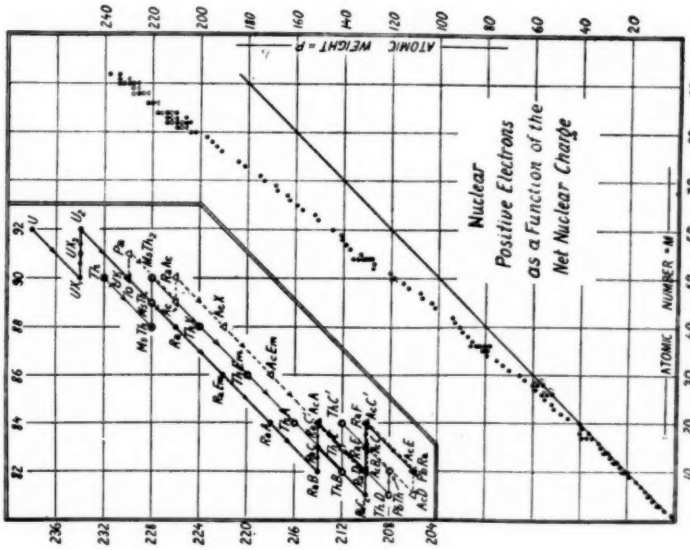
Nuclear
Positive Electrons
as a Function of the
Net Nuclear Charge
ATOMIC WEIGHT = P
ATOMIC NUMBER = M

Fig. 2.

$(p_2e)_2$, that during a series of alpha disintegrations the isotopic number remains constant. Lines of beta disintegration are lines of constant P, along which the number of positive electrons remains constant. The lines of constant N/P radiate from the origin. Most of the other features of this plot are shown more plainly in some of the other diagrams.

The isotopic number is that number which must be added to twice the atomic number to give the atomic weight, and represents the number of neutrons in the nucleus in excess of the formula $(p_2e)_M$. The value of the isotopic number is given by the following equations developed by Harkins:

$$n = P - 2M, \quad (1)$$

$$n = 2N - P, \quad (2)$$

$$n = N - M. \quad (3)$$

As the atomic number increases the isotopic number also increases in general, or the ratio of N/P increases above its minimum value 1/2.

2 AND 3. M, P, AND M, N PLOTS.

In the plot on which M is given on the X, and P on the Y axis, the most abundant atomic species lie on a line with a slope of 2 to 1, or in such atoms the atomic weight is twice the atomic number. All other species of complex atoms are represented by points which lie above this line. It is obvious that the ordinates are given by the equation:

$$P = 2M - n.$$

Fig. 3, which gives the atomic number on the X, and the number of nuclear negative electrons, on the Y axis, resembles Fig. 2 very much, the difference being that the line of minimum slope has the slope 1 to 1. Any point on one of these diagrams is the same number of units above the line of minimum slope on one diagram as it is on the other. This number of units gives the isotopic number, or the number of neutrons present in excess of the formula $(p_2e)_M$. The great simplicity of the relations in Figs. 1 to 3 is due to the fact that the minimum value of N/P which is 1/2, gives the minimum value of P as $2M$, and the minimum value of N as equal to M, since $M + N = P$, or $(M/P) + (N/P) = 1$.

4, 5, AND 6. M, P AND N, ON THE X AXIS; $N/P - 0.5$ ON THE Y AXIS.

Figs. 4, 5, and 6 are very much alike, since the ordinates are the same on all of the three plots. The abscissæ are different, but are very nearly proportional to each other, since M and N are not very different, and P is nearly twice M. Of the three only Fig. 4 will be discussed in detail. In this the *relative negativeness* of the nuclei is given on the Y, and the

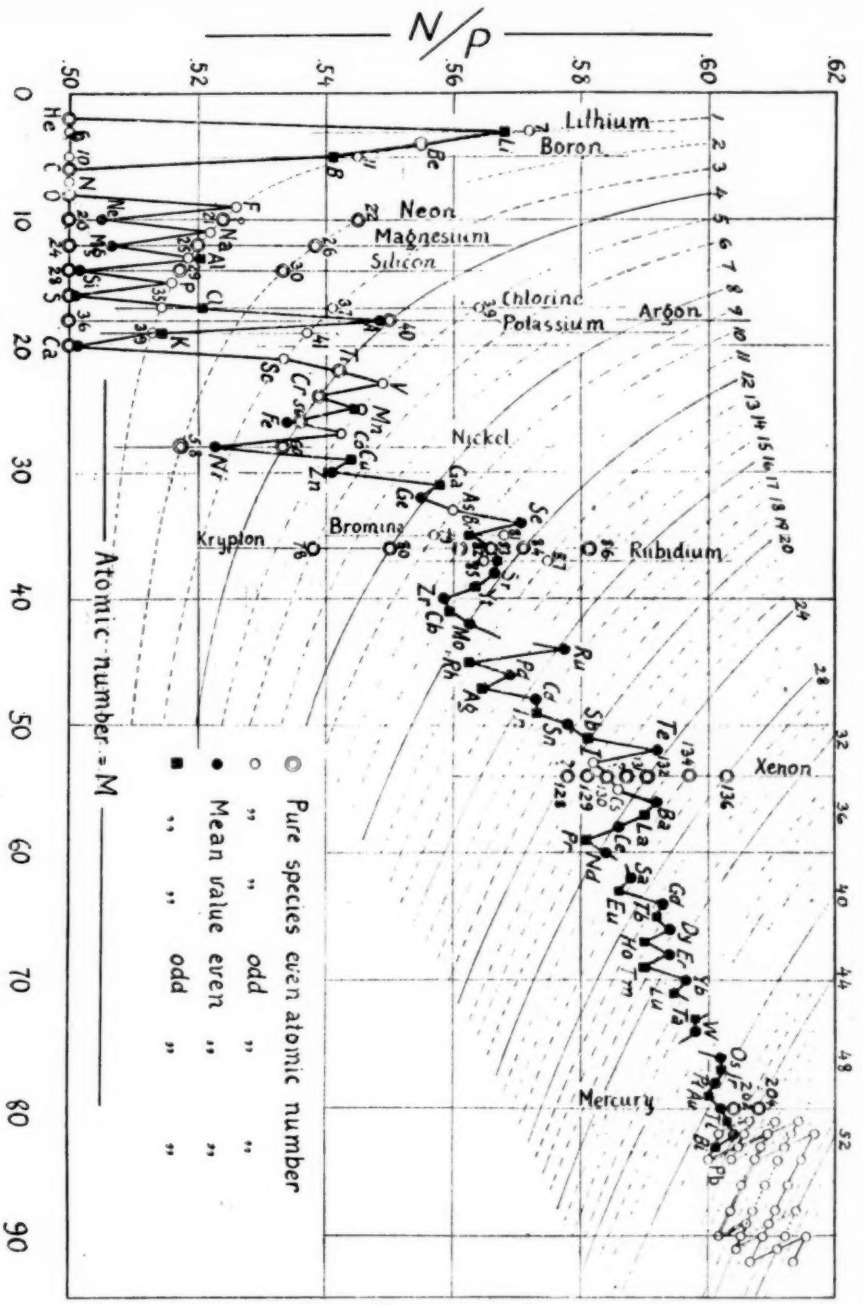

Fig. 4.

The ratio (N/P) of negative to positive electrons in atom nuclei as a function of the atomic number (M). $y = N/P - \frac{1}{2}$; $x = M$.

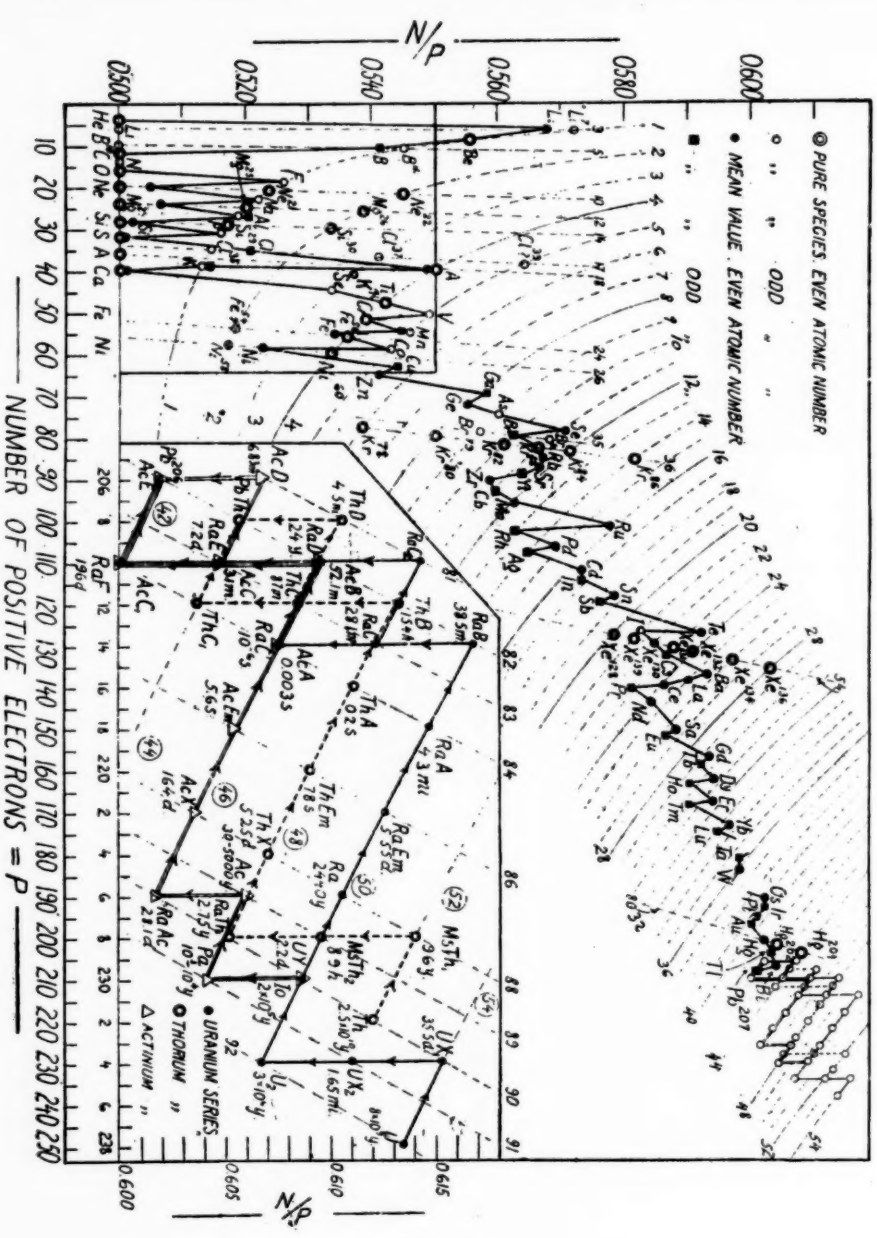

Fig. 5.

Plot showing the ratio of the number of negative to positive nuclear electrons on the *Y*-axis, and the number of nuclear positive electrons on the *X*-axis. Atomic species of zero isotopic number lie on the horizontal line $N/P = 0.5$, which is taken as the *X*-axis of the plot. The isotopic numbers of the other atomic species are given by the numbers of the equilateral hyperbolas.

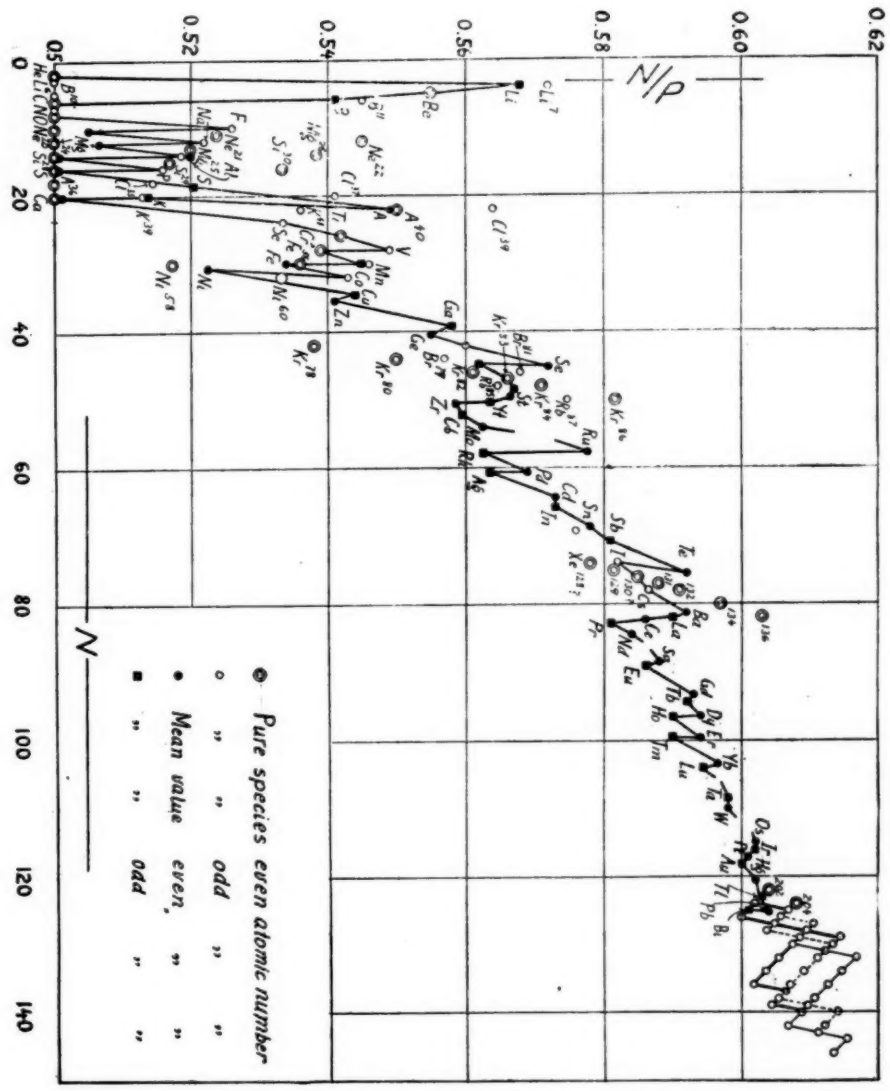

Fig. 6.

Ratio (N/P) of the number of negative to positive electrons in atom nuclei as a function of the number of negative electrons (N).

net positiveness on the X axis. The hypothesis that *the net positive charge on the nucleus exerts a certain self-repulsion, and that this self-repulsion increases with an increase of the charge, provided the relative negativeness of the nucleus remains constant,* has been developed by Harkins.[1] *Stability is secured as the net positiveness increases, by an increase in the relative negativeness.* This is obtained in nuclei built up of alpha particles alone, by the introduction of negative electrons (cementing electrons), used in cementing the alpha particles together. Only cementing electrons are given off in beta disintegrations of the radio-active elements. To a smaller extent an increase in the relative negativeness may be brought about by the addition of groups in which the ratio of N/P is greater than 1/2. Such groups are p_2e_2, p_3e_2, and pe.

Evidence that the relative negativeness (or positiveness) plays an extremely important part in determining stability is found in the relations of the radioactive elements (lower right-hand corner of Fig. 5).[2] This shows plainly that *if atoms of constant net positiveness* are considered, it is found that as the nucleus becomes more negative in the relative sense, the instability with respect to the emission of negative electrons increases (beta period decreases), and the instability with reference to the emission of positively charged particles decreases (alpha period increases). This indicates that even in the closely packed nucleus, unlike charges attract, and like charges repel, or the sign of the effect is the same as at greater distances. Nicholson and other theorists have assumed, without any evidence for their point of view, that this is not true. When radioactive elements of different atomic numbers are compared, no such relation is found, and it is seen that there is a strong indication that the cementing electrons are arranged in pairs, and the alpha particles in groups of varying number, but averaging about four.

The isotopic lines in Fig. 4 have very nearly the form of rectangular hyperbolas, their equation being $2y(2x + k) = k$, in Fig. 6 their equation is $2y(2x - k) = k$, and in Fig. 5 they are rectangular hyperbolas, $xy = k/2$. In these equations k represents the isotopic number. The stability relations may best be expressed by considering one of these lines, for example that for isotopic number 1. The most abundant elements, aluminium, sodium, and Mg_1^{25}, lie near the cusp of the curve. In either direction along the curve, as either N/P or M, that is as either the relative negativeness or the net positiveness, increases, the abundance of the atomic species decreases. Going in either direction along any

[1] Harkins, J. Am. Chem. Soc., *42*, 1971–3 (1920).

[2] Fig. 4, if it gave an enlarged diagram of the radioactive elements, would show this even more simply, since the lines of constant atomic number are vertical, but the two plots are so nearly alike that it seems unnecessary to duplicate this part of the figure.

one of these lines, starting at the position of maximum stability of the nucleus, the instability of the atoms decreases so greatly that after a certain, not very great distance is traversed, no atom is capable of existence for any appreciable time.

It has been shown by Harkins that the nuclear properties are to a considerable extent periodic, the periodicity being between elements of even and odd atomic number. Figs. 4, 5, and 6, indicate that among the light elements (atomic numbers 2 to 32) the mean value of the *relative negativeness* is much higher for elements of odd than for those of even atomic number (except in the case of three transition elements, Be, A, and Sc). Curiously enough, among the elements of higher atomic number, the relative negativeness is in general considerably higher for the elements of even atomic number, since all of the high peaks, and most of the minor ones as well, represent elements of even atomic number. In all of these three figures the lines of constant atomic weight (P) slope more to the left than those for constant atomic number (M), while the lines representing a constant number of negative electrons, slope still more to the left. This is shown by the equations given in Table I.

7. n, $(N/P) - 0.5$ PLOT.

Fig. 7 illustrates the increase of the relative negativeness of the nuclei as the isotopic number increases. All of the extremely abundant atomic species, with the exception of iron and aluminium, are represented by the *point* N/P equal to 0.5, with an isotopic number zero. The region of highest stability has very nearly the form of a parabola, and along any isotopic line the stability decreases on passing vertically higher or lower. As an example the lines showing the net nuclear charge as 92, the number of positive electrons as 238, and the number of negative electrons as 146, which are the values for ordinary uranium, are given. These lines indicate that for a nucleus with any of these three properties, represented by relatively large numbers, to exist, the isotopic number must increase to a sufficiently high value (about 54) to cause the value of the relative negativeness to become sufficiently high (about 0.614) that the repulsion due to large net positiveness may be overcome by the high relative negativeness.

The diagram in the lower right-hand corner of Fig. 7 indicates that during alpha disintegrations the isotopic number remains constant, while the relative negativeness (N/P) increases slightly. After several changes the nucleus becomes so negative in the relative sense that positively charged particles no longer leave it, but negative electrons are shot off. Each beta disintegration lowers the isotopic number by

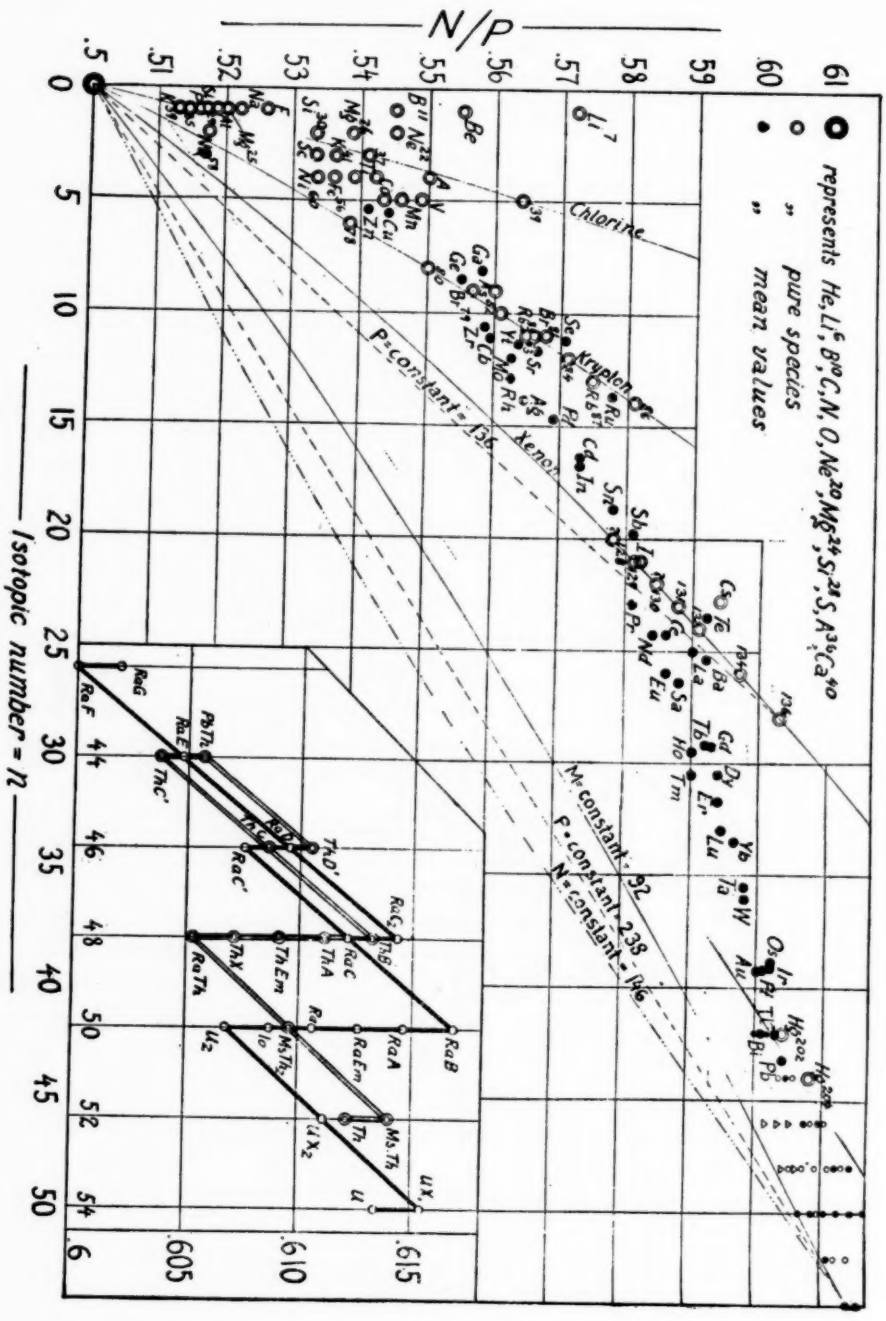

Fig. 7.

Ratio (N/P) of the number of negative to positive electrons in atom nuclei as a function of the isotopic number (n).

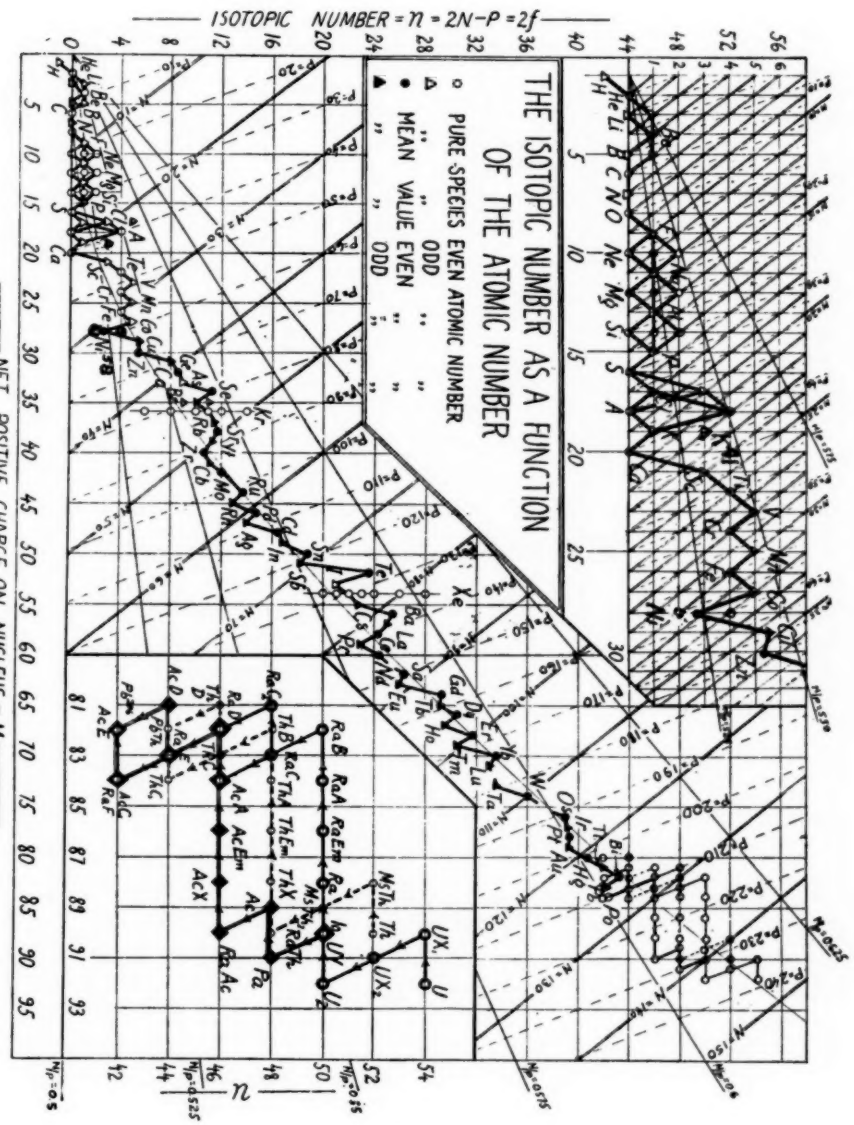
ISOTOPIC NUMBER = n = 2N−P = 2f
THE ISOTOPIC NUMBER AS A FUNCTION OF THE ATOMIC NUMBER
PURE SPECIES EVEN ATOMIC NUMBER
" ODD " "
MEAN VALUE EVEN " "
" ODD " "
NET POSITIVE CHARGE ON NUCLEUS = M
n

Fig. 8.

On this plot constant values for (1) the net positive charge on the nucleus, M; (2) the number of hydrogen nuclei or positive electrons in the nucleus, P; (3) the number of nuclear negative electrons, N; (4) the isotopic number, n; and (5) the ratio N/P, are all represented by straight lines.

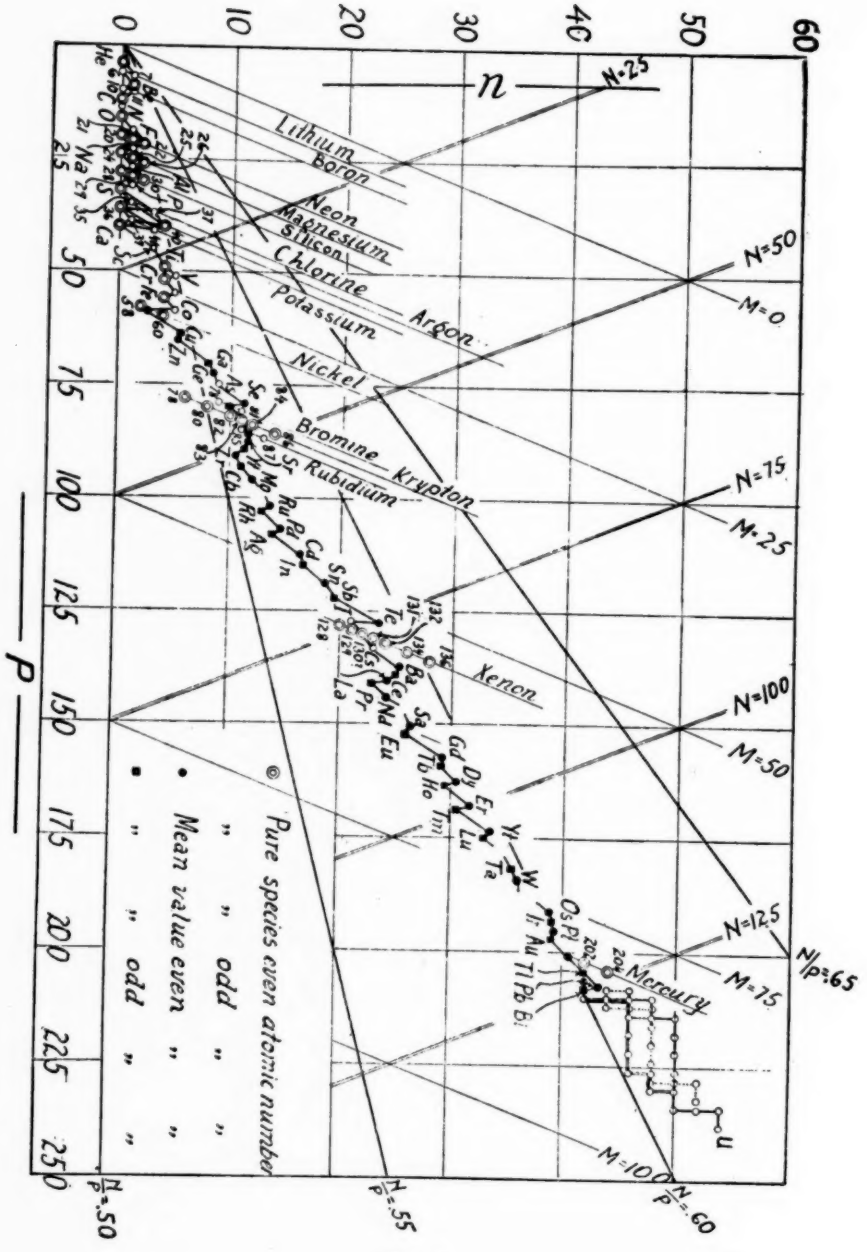

Fig. 9.

Isotopic number as a function of the number of positive electrons.

two, and in this region decreases the relative negativeness slightly more than two alpha disintegrations. It may seem strange that the loss of one negative charge changes the numerical value of the ratio N/P more than two losses of doubly charged positive particles, but the reason for this is obvious, since the loss of an alpha particle decreases both P and N. It is apparent that beginning with uranium, 27 beta changes would be sufficient to bring the plot to the origin, independently of the number of alpha changes, so this is the highest number of beta changes of this type possible for any known atom.

8, 9, AND 10. M, P, OR N ON THE X AXIS, n ON THE Y AXIS.

Figs. 8, 9, and 10 represent the isotopic number on the Y axis. All of them have the property that constant values of all of the five variables are represented by straight lines; four, P, M, N, and n, by sets of parallel straight lines, and N/P by lines radiating from the origin. The heavy lines in the radioactive region indicate the paths of the decompositions, but in the remainder of the diagram are only intended to bring out the position of the region of highest stability, which takes on very nearly the form of an hyperbola. A part of this figure has been considerably enlarged, and is shown in Fig. 11, which will serve to indicate the relations more clearly.

In figure 11 the lines for four of the variables, P, N, M, and n, all meet at every corner. Each such corner corresponds to the existence of a *possible* isotope, but not every corner corresponds to a condition of stability. From the general theory already presented it is to be expected that most of the corners which are filled will represent an *even number* of negative electrons. This means that when the atomic number (M) is even, the isotopic number (n) is also even, and when the atomic number is odd, the isotopic number is also odd. *Thus in general the atomic number, isotopic number, and number of positive electrons, all match in the sense of oddness or evenness,* that is all of these numbers are either even, or else they are all odd. In the range of this figure, 3 out of the 31 atomic species thus far found, do not follow this rule. The secondary relation here revealed is that in a small fraction of the known atomic species P and N are both odd together. Only in extremely exceptional cases (less abundant isotopes of Li and B) is N odd, and P even.

Figure 11 has exactly the characteristics which it would have if across it had been plotted the tracks of four radioactive disintegration series, and it gives ample evidence that the light atoms from carbon to zinc as well as the heavy atoms are built up from alpha particles of mass 4, for along each isotopic line the atomic number jumps by 2 and the atomic weight

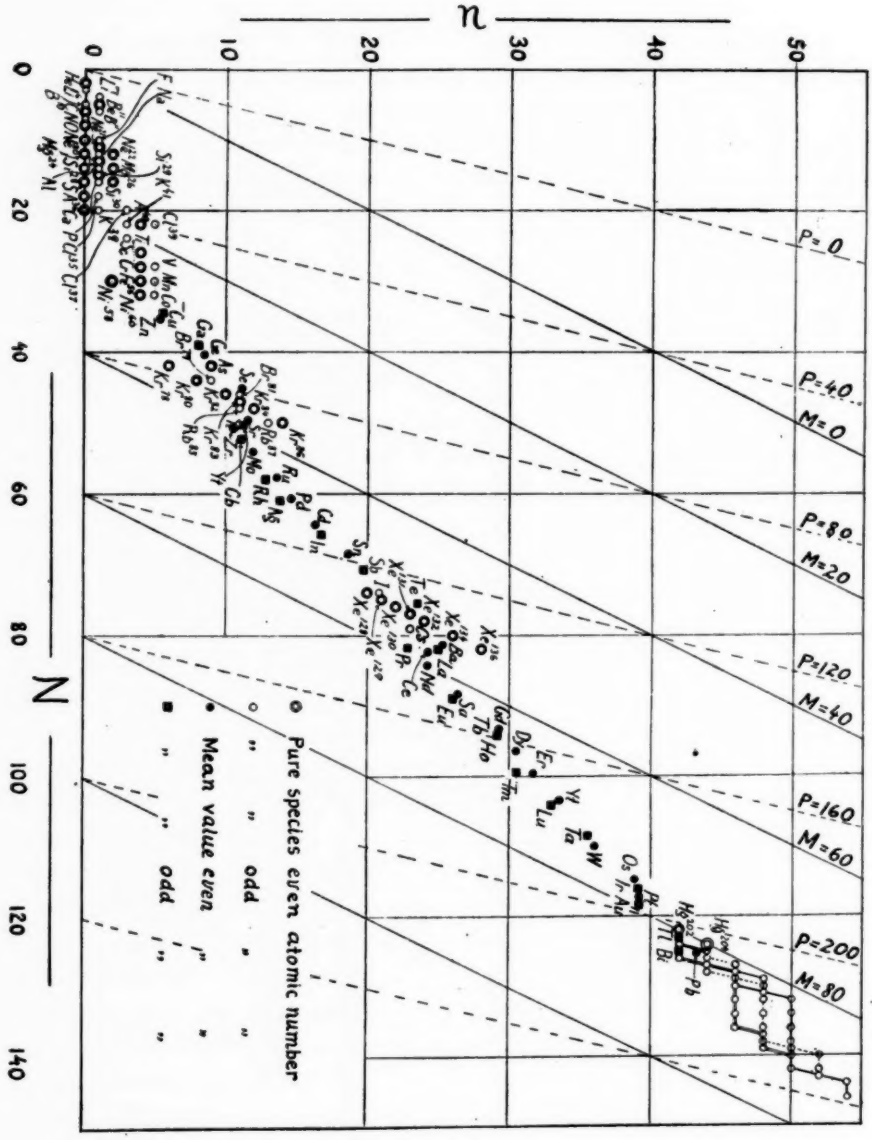

Fig. 10.

Isotopic number (n) as a function of the number of negative electrons (N).

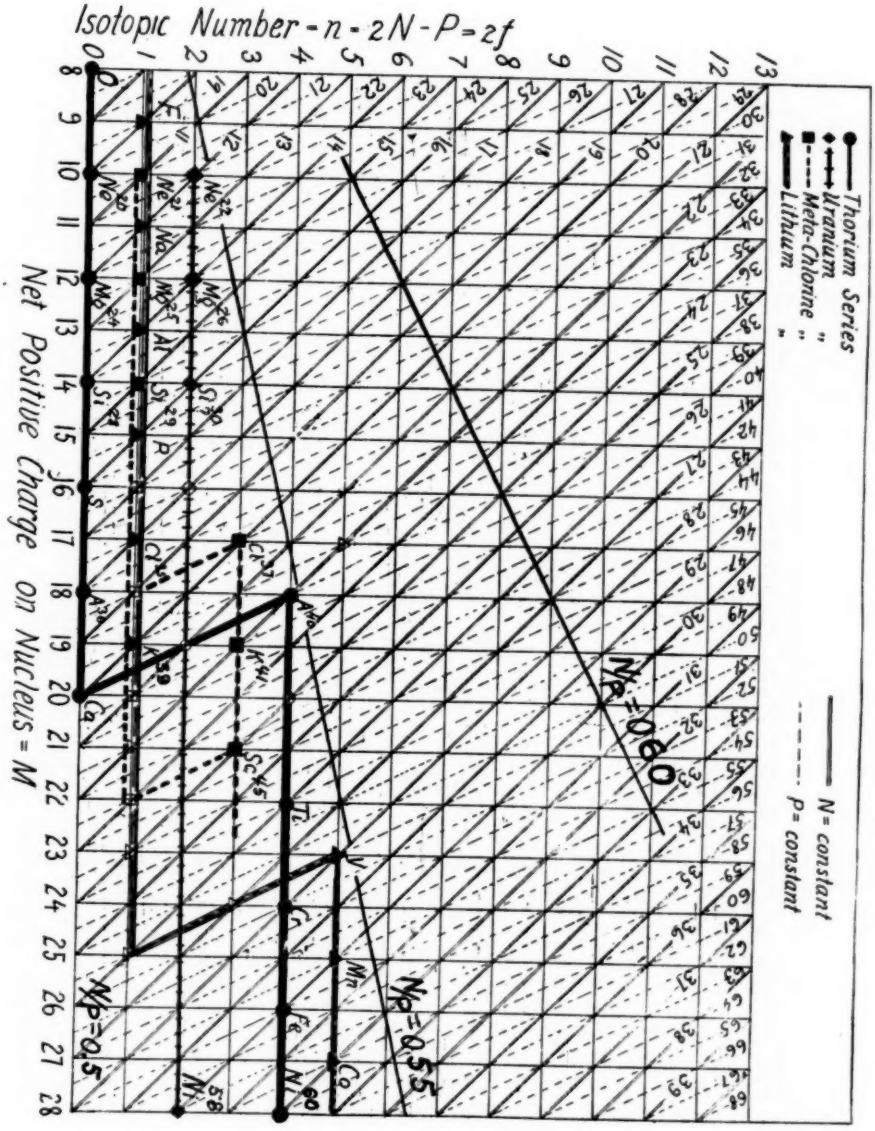

Fig. 11.

(Enlarged section of Fig. 8.) Isotopic number as a function of the net nuclear charge (*M*)

by 4. Only between fluorine and phosphorus do two of these series become intermingled. Out of the 14 atomic species depicted as belonging to the Helium-Thorium Series, only two remain undiscovered. One of these, K^{41}, probably does not exist in quantities large enough to be easily discovered. The other is Ca^{44}. The form of such a plot is determined by the stability relations of the atoms. The figures of this paper suggest that the light atoms, as well as the heavy ones, both build up, and disintegrate. The ratio N/P changes much more markedly with the isotopic number among the light than among the heavy atoms, so the range of the isotopes in terms of the isotopic number or atomic weight, is much less when the atomic number is low. It is of interest to note that in Fig. 11, while the value 0.55 for the value of N/P is practically attained three times, in no place is it exceeded. While in this range atoms with values of N/P higher than this limit may be discovered, it is now apparent from the atomic weights and the general relations involved, that no such atomic species will be at all abundant.

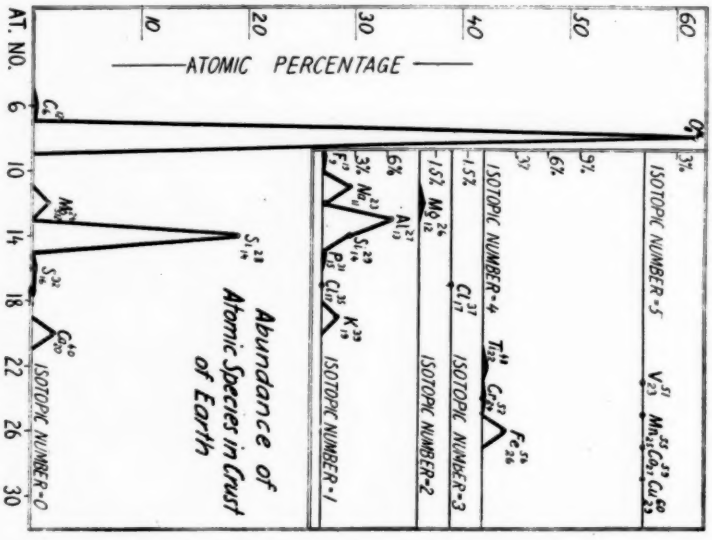

Fig. 12.

Shows the periodic variation in the abundance of the atomic species of each isotopic number.

That the abundance of the atoms of any isotopic number is periodic, is shown by Fig. 12. The abundance is greatest for isotopic number 0, and decreases gradually to a minimum in isotopic number 3, rises to a secondary maximum in isotopic number 4, and again decreases. Thus there is also a periodic variation of the abundance of the atoms in the isotopic numbers, which gives a maximum with each fourth isotopic

number. While these maxima probably become much less prominent as the atomic number increases, their prominence in the range of low atomic numbers is strongly suggestive that the periodicity by 4 is due to the fact that 4 is the mass of the alpha particle.

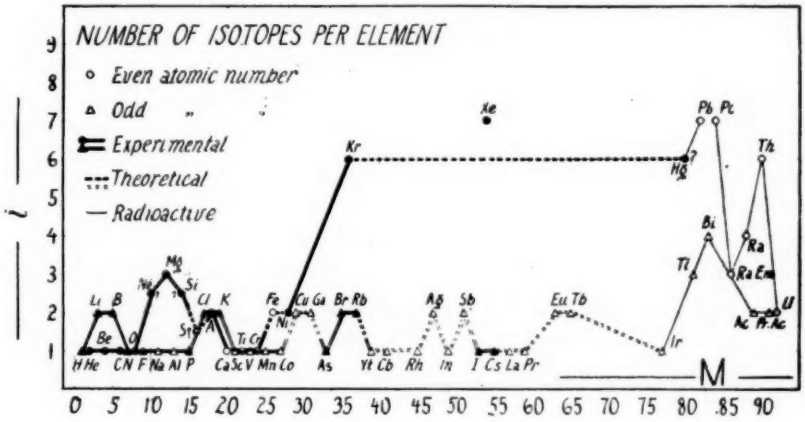

Fig. 13.

Approximate number (i) of isotopes per element.[1]

[1] This figure plots the number of isotopes per element thus far discovered, using inked-in symbols. For elements whose isotopes have not been determined a rough estimate of the probable number is given. This number is based upon the assumption that the chemical atomic weight is entirely exact. In so far as this assumption is not justified, the number of isotopes predicted cannot be expected to be correct; and it is well known that many of the chemical atomic weights are very much in error. This is illustrated by the case of antimony, the atomic weight of which has been changed more than a unit by the most recent determinations. The number of isotopes in neon and silicon is plotted as 2.5, an impossible number, to indicate that Aston's experimental determinations are indefinite, giving in each case two isotopes, with a third doubtful. While the number of isotopes plotted for the radioactive elements is greater than for the preceding elements, this is only because the experimental means used for their detection is much more delicate. While Aston was able to find only one atomic species for sulphur, the chemical atomic weight indicates that sulphur consists of at least two isotopes. To show the relations properly the plot should be three-dimensional, and should give the abundance of each isotope. For example, in the two-dimensional diagram lithium, with only 6 per cent. of the higher isotope, is given the same rating as chlorine with 23 per cent. and bromine with about 50 per cent., which gives a false impression unless these facts are kept in mind. The designation of indium, columbium, yttrium, lanthanum, and praeseodymium as consisting of only one isotope each, is probably without meaning, since in most of these the atomic weight is not known with sufficient accuracy as to give a basis for a definite prediction. On the other hand the atomic weights of silver and copper are known with sufficient precision as to justify the *prediction that each of these elements consists of two isotopes*. It is of course possible that three isotopes may exist, but the number of isotopes sufficiently abundant to be detected by the positive ray method in its present degree of sensitiveness, is in general not greater than two for elements of odd atomic number.

The most important feature of this plot is that it illustrates the fact that *the number of isotopes is in general much higher for elements of even than for elements of odd atomic number, especially for elements of atomic numbers greater than 30*. This is exactly in accord with the

Figure 13 shows the way in which the number of isotopes per element varies with the atomic number. It will be seen that the relations are exhibited most easily when separate curves are drawn for the elements of even and of odd atomic numbers. The lines represent only the most general form and not the details of the numerical relations.

While Aston did not find a higher isotope of sulphur, there is little doubt of the existence of such an isotope, which would have an atomic weight of either 34 or 33. Also there is little doubt that a higher isotope of calcium (possibly 42 or 44 atomic weight) and a lower isotope of iron (probably 54) exist. The stability relations contain specific factors of such importance that it is impossible to tell exactly the relative abundance of such isotopes. However it may be pointed out that Harkins predicted the existence of the 6 and 7 isotopes of lithium, the 10 and 11 isotopes of boron, and the 24 and 26 isotopes of magnesium without making a single error in the predictions, but failed to predict the existence of the 25 isotope of magnesium, for which the relations are much more specific.

UNIVERSITY OF CHICAGO,
September 12, 1921.

predictions from the theory of the stability of atom nuclei as presented by Harkins in various papers published in the years 1915 to 1917. (It is of interest to note that the number of isotopes of element 30 (zinc) has just been found to be 4 by Dempster. Thus the number of isotopes increases exactly at the point predicted by Harkins in the year 1915.)

TIME AND PRESSURE MEASUREMENTS IN THE CORONA.

BY CHARLES S. FAZEL.

SYNOPSIS.

Pressure Effects Due to the Corona Discharge in Dry Air.—The discharge took place from a fine wire inside a concentric tube. By means of a sensitive differential gage it was found that the pressure at the tube was 0.004 cm. of water higher than at the wire, *for both A.C. and D.C. discharges.* Studies made with a recording mica diaphragm gage showed that on starting the D.C. discharge the pressure rose gradually, reaching in about 1½ seconds a limiting value proportional to the current. The curves for A.C. discharges were the same except that superposed on the D.C. curves were periodic pressure changes with twice the frequency of the alternating voltage and with an amplitude of 0.3 cm. of water. When the wire was heated without the discharge, with either A.C. or D.C. current, the pressure curve took about 20 seconds to reach its limiting value and showed no periodic variations. If when the steady state was reached the corona discharge was started, the pressure either decreased to a lower limiting value, or increased to a maximum and then decreased to a limiting value lower than before or higher than before, depending on the voltage of the discharge. Evidently several effects are superposed in this case. The experiments show the existence of characteristic pressures in the corona in addition to the pressure due to the heating of the gas by the current through the wire.

INTRODUCTION.

THE gas pressure developed by the corona discharge has been studied by Farwell,[1] Kunz,[2] Warner,[3] Arnold,[4] and Tyndall.[5] Warner has shown that the corona pressure developed is proportional to the corona current. He has suggested that there was a true corona pressure distinct from that due to pure thermal effects and as an explanation has suggested the ionization theory. On the other hand, Arnold and Tyndall have contended that the effect was due to the heat developed.

The tube used by Tyndall had a diameter of 2.2 cm. and the wire of a diameter of .006 mm., while in Warner's work the tube was 4.5 cm. in diameter and the wire had a diameter of .019 cm. In addition the current used by Tyndall was of the order of magnitude of 10^{-3} amps. (unless there is a misprint in his article as some of his other data would indicate), while Warner used a current of magnitude of 10^{-5} amps. These differences could make the pressure evolution due to heat the

[1] Proc. A. I. E. E., 33, 717.
[2] PHYS. REV., 8, 28.
[3] PHYS. REV., 10, 483.
[4] PHYS. REV., 9, 93.
[5] Phil. Mag., 35, 483.

predominant factor in one case and the pressure due to the corona in the other.

The following experiments were undertaken to see whether there existed a characteristic corona pressure. The development of pressure due to heating the gas by the passage of the current could not be called such a pressure. But a pressure due to ionization or ionic wind would come under that class.

I. The Pressure Distribution Within the Tube.

In view of the possibility that the pressure might be due to the ionic wind the pressure difference between the walls of the tube and the wire was measured by a differential gage of the Wahlin[1] type. A special gage was constructed so that the columns over the liquids were as small as possible and the ratio of the cross sectional areas of the tubes was about one to ten.

One side of the gage was connected to the outside of the corona tube while the other was attached to a glass tube which could be moved in to the center of the tube. The connections from the tube to the gage were kept as short as possible. The gage thus read the difference in pressure between the walls of the tube and the neighborhood of the wire. Considerable difficulty was experienced until the air was dried very thoroughly by passage through sulphuric acid and calcium chloride. The presence of water vapor lowers the voltage at which an arc will form and tends to decrease the corona pressure difference.

With carefully dried air and the sensitive gage mentioned above a pressure difference between the wire and the tube of about .004 cm. of water was detected at 12,000 volts D.C. The walls of the tube were always at the higher pressure whether the wire was positive or negative. The apparatus was not sensitive enough to tell whether there was any difference in the magnitude of the pressure difference when the wire was positive or negative.

Tyndall[2] has calculated from Chattock's values for the mobility that the electric wind should give rise to a pressure difference of .003 cm. of water between the wire and the tube. It would therefore seem that the pressure just measured was due to the ionic motion.

Even with this difference it is still difficult to see how such a small air movement could accomplish the cooling which Tyndall attributes to it. The motion of the air due to this small pressure difference would last for a short time and could not produce very much cooling, especially on account of the small specific heat of air.

[1] Bull. University of Illinois Eng. Exp. Sta., No. 112, p. 25, 1919.

[2] Phil. Mag., 35, 264.

Fig. 1.

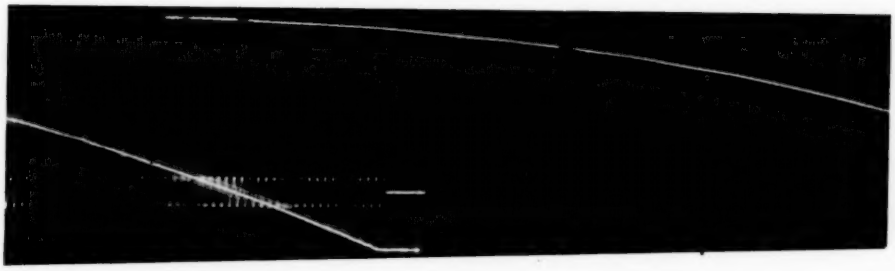

Fig. 3.

Fig. 4.

Fig. 6.

CHARLES S. FAZEL.

II. Corona with the Manometric Flame.

It would seem possible to distinguish between the corona pressure and the pure heat effects on the basis of the time taken to reach the steady state. In order to study this a corona tube was supplied with a sixty-cycle alternating potential of about twelve thousand volts. The outside of the corona tube was grounded to eliminate electrostatic effects. A connection was then made from the tube to a manometric capsule.

Using this apparatus a new phenomenon was observed. It was found that the flame showed a periodic pressure change of twice the frequency of the impressed electromotive force. By pinching the rubber tube connecting the corona tube with the capsule the vibrations of the flame stopped. Grounding the capsule and other parts of the apparatus produced no effect on the flame. A sample record is shown in Fig. 1. The upper is the pressure while the lower is a manometric flame attached to a telephone which carries part of the same current which actuated the transformer. For the lower flame the length of each spot of light represents a one hundred twentieth of a second (for the remainder of the cycle the flame is extinguished). It should be noticed from the upper flame that the pressure change in the corona tube is able to follow a frequency of one hundred and twenty cycles per second, which is much faster than any of the pressure changes observed before in the corona.

It was noticed that the flame was greatly affected on the make and break of the current. In fact it was often extinguished at these times if it was in its most sensitive condition. In order to investigate this phenomenon a pressure gage was built which would give readings of pressure rather than change of pressure with the time. The results obtained with this gage will be discussed later (Part III.).

The heating of the gas by an alternating current passed through the central wire was tried to see whether the alternating pressure might not be due to the alternate heating and cooling. With this arrangement the flame did not show any oscillations even though the wattage used was more than ten times that used in the corona.

In case the central wire was heated by the alternating current as above and at the same time the corona was put on the tube the flame behaved in exactly the same way as it did when the wire was not heated. That is, the flame showed a periodic pressure of twice the frequency of the impressed electromotive force. This indicates that the variations in the pressure depend on having a varying potential difference between the wire and the outside of the tube and not on the temperature of the wire nor in the variations of its temperature due to the alternations of the current.

With the same apparatus as used on the alternating current corona, the direct current corona was investigated for an oscillatory pressure. With the direct current on the corona tube no oscillations could be detected except irregular fluctuations with a period of about a second which were probally due to variations of the voltage of the machines. With the spark in series with the tube no oscillations could be detected using the flame and the rotating mirror.

III. Corona with the Pressure Gage.

The experiments described above with the manometric flame showed that there must be effects on the make and break of the current which could not be shown with this flame. In order to study these effects more fully a quick-acting recording pressure gage was constructed.

This gage consisted of a diaphragm of mica which was placed across the end of a corona tube having a wire which ran about seven-eighths of the full length. Attached to this mica plate was a silk thread held taut by a spring. A small mirror was supported on a vertical thread by one edge and the other edge was attached to a horizontal thread. Any motion of the mica diaphragm was thus transmitted to the mirror which gave a deflection of a beam of light. The gage as used gave a five-centimeter deflection for a pressure of one centimeter of water. The natural period of the gage as used in most of the experiments was in the neighborhood of 700 vibrations per second. The current in the primary of the transformer was recorded by an oscillograph. A diagram of the apparatus is shown in Fig. 2.

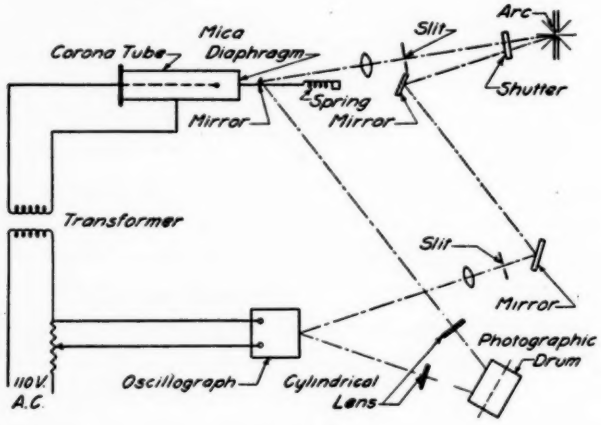

Fig. 2.

Using such a gage, Fig. 3, shows the increase in pressure in a corona tube when an alternating current of sixty cycles is thrown on. The

voltage is about nine thousand volts at the peak. The halo on the rising line is due to diffraction of the beam of light at the slit. The sine curve is the sixty-cycle wave representing the current. The record begins about one fourth of the distance from the left-hand side and reads right to left. There is some overlapping due to the shutter not being closed quickly enough.

It is evident that there are present the oscillations shown by the flame having half the period of the impressed electromotive force, but these are superimposed on a gradually increasing pressure which reaches a constant value in about a second and a half. There are two distinct types of pressure here, one which is able to follow variations of one hundred and twenty cycles per second, and another which requires more than a second to reach its value. The rapid pressure variations are such a large value that they cannot be the electric wind pressure. The "electric wind" pressure should have a magnitude of about .005 cm. of water while the alternating pressure change has been found to have a value of more than .3 cm. of water.

An attempt was made to study in greater detail the steady state of oscillation reached at the end of Fig. 3. This was done by the use of a thinner diaphragm and greater magnification which was obtained by decreasing the width of the mirror and increasing the distance from the mirror to the film. It was found that this brought the free period of the gage so near to the period of the oscillations which were being studied that satisfactory results were not obtained.

The variations in pressure which follow the breaking of the primary current of the transformer were studied and Fig. 4 shows the result. There is a slow dying away of the pressure which corresponds to the slow increase shown in Fig. 3. However, there is a new phenomenon as the oscillations persist with their original frequency and die out very slowly. These cannot be due to the natural frequency of the diaphragm or measuring system on account of the difference in frequency nor could it be the natural frequency of the electrical system as it would be in the millions of oscillations per second. This might be due to reverberation as the cylindrical wave—similar to a sound wave—would persist until its energy was absorbed by the walls. This point however requires further study.

IV. Heat Effects in the Corona Tube.

In order to study the effect of heat alone on the pressure development an alternating current was sent through the central wire and the increase of pressure observed. It was found that this pressure increase was so

slow that it could not be recorded on a photographic film with the apparatus at hand and so the results were obtained by visual observation. It was found possible to reproduce these observations within half a per cent., at the upper values and so the method was considered satisfactory.

Fig. 5 shows the curves for several different currents through the wire.

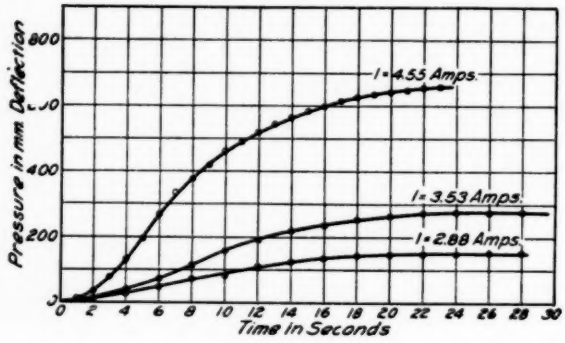

Fig. 5.

It will be seen that the maxima are not reached until the wire has been heated for more than twenty seconds, while Fig. 3 showed that in the alternating current corona the maximum is reached in less than two seconds. Further, the time required to reach the maximum does not depend upon the current to any marked extent. The maximum pressure reached depends on the current through the wire as would be expected. There is a marked difference in form of curves in Fig. 5 from those of Fig. 3. There would be no difficulty in distinguishing this type of pressure from the very rapid type shown in Fig. 1 and Fig. 3. It therefore seems possible to distinguish between the pressure due to the heat evolved and the pressure due to the corona.

V. Relation between Heat and Corona.

Tyndall[1] describes an experiment in which he had a tube with a wire heated by a current such as that used in the preceding experiments. After the pressure due to the heated wire had reached a steady value he threw on the corona and observed a pressure decrease. A similar experiment was performed recording the slow part by visual observations and the pressure changes when the corona was first put on by means of the recording pressure gage. The record of the pressure changes when the corona was first put on is shown in Fig. 6. The results of the whole experiment are shown in Fig. 7.

It is seen that as soon as the corona is thrown on there is a very quick

[1] Loc. cit.

increase in pressure followed by a slow decrease to another constant value below the original. Tyndall's failure to observe the initial increase may have been due to the use of a rather slow acting pressure gage, or to the relation between heat and corona.

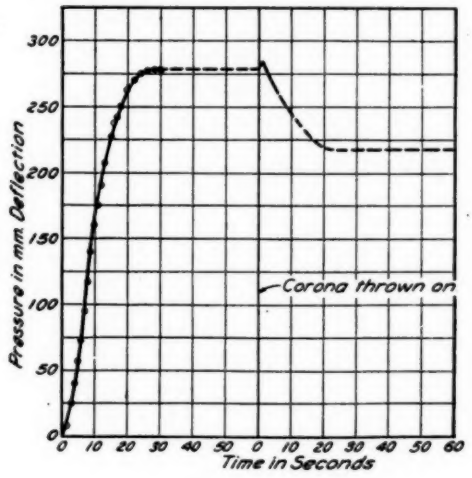

Fig. 7.

A study was then made of the maximum excursions on either side of the steady state by varying the voltage across the transformer. A number of records similar to Fig. 7 were made. The value of the sharp peak reached after the corona was thrown on, was plotted above the axis in Fig. 8 with the voltage of the transformer as abscissa. Likewise the

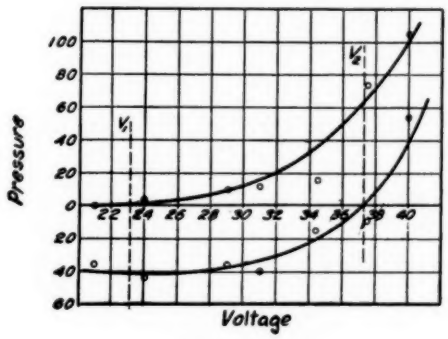

Fig. 8.

final pressure reached at the end of the experiment was plotted below the axis in Fig. 8.

From these curves it is seen that it is possible to find a voltage V_1, below which there is a decrease in pressure without any appreciable

initial increase. It is possible that Tyndall's experiments were conducted below this voltage. Between the voltage V_1 and V_2 there is an increase in pressure followed by a decrease to a value below the original pressure. Above the voltage V_2 the pressure increase is followed by a decrease but to a value above the original pressure. This shows that there is a superposition of several effects.

VI. SUMMARY.

The gas pressure phenomena in the alternating and direct current corona have been studied. It has been found that there are four of these phenomena in the corona tube: first, there is a pressure difference which appears between the tube and the wire of the order of magnitude of .005 cm. of water; second, a pressure of the order of magnitude of .3 cm. of water which is able to follow variations of one hundred and twenty cycles per second. Third, there is a pressure which develops in about a second and a half. This has been carefully studied by Warner who showed that it was proportional to the current provided that the heating was kept small so that it would not obscure the effect. Fourth, a pressure due to the heating of the gas which is much slower than any mentioned above.

The author desires to express his thanks to Dr. Jakob Kunz for advice and aid throughout the experiments and to Professor A. P. Carman for facilities furnished.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
August, 1920.

ON THE PRESSURE IN THE CORONA DISCHARGE.

By Jakob Kunz.

Synopsis.

Theory of Pressure Effects Due to the Corona Discharge, in Terms of Ionic Mobility.—The characteristic pressure effect is an excess pressure of from 1 to 3 cm. of water inside a tube concentric with the discharge wire. Assuming that the momentum given the ions by the electric field is transferred to the gas, the author shows that the excess pressure is $i/4\pi u$, where i is the current per unit length of wire and u is the mobility. Using this expression, the *positive mobilities in* H_2, N_2, CO_2, O_2 *and* NH_3 *are computed* from the observed pressure differences, and come out respectively 1.51, 0.50, 0.16, 0.23 and 0.31 times 10^{-2} cm./sec. per volt/cm. The first three values are about half those measured by Hess in the wind of ions from radioactive substances, while the value for O_2 is only one eighth, the low value being perhaps due to ozone. The results so far refer to the mean mobility. Assuming that there are two types of ions, the *percentage of heavy ions* comes out about 13 for O_2. The time for the pressure to rise to its limiting value is computed and comes out in rough agreement with the measurements of Fazel; and an explanation is suggested for the form of the pressure curves obtained by Fazel with A.C. discharges.

IT has been shown by E. H. Warner[1] that the initial pressure increase in the corona discharge is proportional to the current, that it varies in the different gases from a small value in hydrogen to higher values in nitrogen, ammonia, oxygen and reaches the highest value in carbon dioxide for a given current. A. M. Tyndell[2] has tried to explain the phenomenon in question as a pure heat effect. He has made an experiment moreover in which the central wire was heated and thereupon the potential difference applied. Instead of increasing, the pressure decreased. This phenomenon is apparently connected with the effect observed by J. W. Davis, that in the rectification of alternating currents through the corona discharge in hydrogen, the wire which was red hot, became dark as soon as the corona appeared. In the previous investigation by means of alternating currents and an oscillograph, C. S. Fazel showed that even in this experiment of Davis and Tyndall the pressure at first in a very short time interval increases and then rapidly decreases. So far the following phenomena have been observed:

1. A very small pressure difference, hardly measurable, between the central wire and the outer cylinder.

[1] Physical Review, Vol. 10, p. 483, 1917. See also the corona discharge by E. H. Warner and J. Kunz, University of Illinois Engineering Experiment Station Bulletin No. 114, 1919.

[2] Phil. Mag., Vol. 35, p. 261, 1918.

2. A pressure increase proportional to the current in the D.C. corona, which appears in about 1.5 seconds after the beginning of the corona. This pressure increase may easily amount to 3 cm. of water.
3. With alternating current a varying pressure increase occurs of about .3 cm. of water with a frequency $2n$ when the frequency of the A.C. is equal to n. These pressure fluctuations are superimposed on the effect mentioned before.
4. A pressure decrease which occurs, when direct current or alternating current corona arises from a hot central wire, after an initial pressure increase.
5. A pressure increase due to Joule's heat which can readily be separated from the effect (2).

The principal phenomenon is the pressure increase mentioned under (2) which we shall try to explain by means of the small mobilities of ions which have been measured by Victor F. Hess [1] in the wind of ions emanating from radioactive substances.

The central wire of radius R_1 in the coaxial corona cylinder of radius R_2 has a positive charge and emits in the corona discharge n positive ions per unit length and per unit time. During the time interval dt every positive ion travels through the distance dr with the velocity $v = dr/dt$. Let the electric force at the point r be E, the charge of the ion e, then the increase of the electric impulse during dt is equal to $eEdt$. We assume that this momentum be transmitted to the molecules of the gas so that a pressure difference dp occurs between r and $r + dr$. Since n ions per unit time cross the surface of the cylinder $2\pi r$, then we get: $neEdt = dp2\pi r$. But $ne = i$ which is the corona current per unit length, hence

$$iE\frac{dr}{v} = dp2\pi r.$$

According to the definition of mobility u of the ions, we have

$$v = uE;$$

hence

$$\frac{i}{u}dr = dp2\pi r \tag{2}$$

or

$$\frac{i}{2\pi u}\frac{dr}{r} = dp \tag{3}$$

or

$$\frac{i}{2\pi u}\log\frac{R_2}{R_1} = p_2 - p_1. \tag{4}$$

[1] Sitzungsberichte der Akademie der Wissenschaften von Wien. Math. Abt., 128. Bd. Heft 6, 1919; 129. Bd. Heft 6, 1920.

The pressure difference between the cylinder and the wire is proportional to the current and inversely proportional to the mobility of the ions. If, however, we attach to the corona cylinder an open manometer, we measure the pressure difference between the inner side of the cylinder and the outer pressure $p_2 - p_0$ and not $p_2 - p_1$. We determine the pressure difference $p_2 - p_0$ in the following way:

$$\int_{R_1}^{r} dp = \frac{i}{2\pi u} \int_{R_1}^{r} \frac{dr}{r},$$

$$p - p_1 = \frac{i}{2\pi u} (\log r - \log R_1). \tag{5}$$

The conservation of mass gives the following equation:

$$\int_{R_1}^{R_2} p 2\pi r dr = p_0 \pi (R_2^2 - R_1^2). \tag{6}$$

From (5) we substitute p in (6) and carry out the integration.

$$p_1 \pi (R_2^2 - R_1^2) - \frac{i}{2u} \log R_1 (R_2^2 - R_1^2) + \frac{i}{u} \int_{R_1}^{R_2} r \log r dr = p_0 \pi (R_2^2 - R_1^2).$$

or

$$p_1 = p_0 + \frac{i}{2\pi u} \log R_1 - \frac{i}{4\pi u} \left[\frac{R_2^2 \log R_2^2 - R_1^2 \log R_1^2}{R_2^2 - R_1^2} - 1 \right]. \tag{7}$$

We have moreover:

$$\int_{r}^{R_2} dp = \frac{i}{2\pi u} \int_{r}^{R_2} \frac{dr}{r} = \frac{i}{2\pi u} (\log R_2 - \log r) = p_2 - p. \tag{8}$$

We substitute this last p in equation (6) and obtain:

$$p_2 = p_0 + \frac{i}{2\pi u} \log R_2 - \frac{i}{4\pi u} \left[\frac{R_2^2 \log R_2^2 - R_1^2 \log R_1^2}{R_2^2 - R_1^2} - 1 \right]. \tag{9}$$

From (7) and (9) we obtain again equation (4). The pressure difference $p_2 - p_0$ is now given by the expression:

$$p_2 - p_0 = \frac{i}{2\pi u} \left[\log R_2 - \left(\frac{R_2^2 \log R_2 - R_1^2 \log R_1}{R_2^2 - R_1^2} - \frac{1}{2} \right) \right].$$

In our experiments R_2 and R_1 had the following values:

$$R_2 = 2.25 \text{ cm.}, \quad R_2^2 = 5.05, \quad \log R_2 = 0.81,$$
$$R_1 = .01 \text{ cm.}, \quad R_1^2 = 10^{-4}, \quad \log R_1 = -4.6.$$

Therefore approximately

$$\frac{R_2^2 \log R_2 - R_1^2 \log R_1}{R_2^2 - R_1^2} = \log R_2$$

and

$$p_2 - p_0 = \frac{i}{4\pi u}$$

or

$$u = \frac{i}{4\pi(p_2 - p_0)}. \tag{10}$$

The total current measured in the corona tube of length l was I, hence $i = I/l$ and

$$n = \frac{I}{4\pi l(p_2 - p_0)} = \frac{I}{4\pi l \Delta p}. \tag{11}$$

This pressure increase Δp is assumed to be due entirely to the corona wind and not partly to the heat of Joule. This latter pressure increase, according to the measurement of Warner, is only about 1/2 per cent. of the observed pressure increase in the first second. The necessary small correction is already contained in the values of Δp that are used in the calculation of the mobilities.

We apply formula (11) at first to the straight lines of Fig. 45, page 85 of the bulletin of Warner and Kunz, in order to determine the ratio of the mobilities of the ions in various gases. We choose always the same current $I = 2.10^{-4}$ amp. and obtain the following ratios:

$$\frac{U_{H_2}}{U_{N_2}} = \frac{p_{N_2}}{p_{H_2}} = \frac{1.3}{0.4} = 3.2$$

while Hess gives 3.5.

$$\frac{U_{H_2}}{U_{CO_2}} = \frac{4.2}{0.4} = 10.5;$$

Hess gives 8.3

$$\frac{U_{H_2}}{U_{NH_3}} = \frac{2.2}{.4} = 5.5$$

$$\frac{U_{H_2}}{U_{O_2}} = \frac{3}{.4} = 7.5.$$

These ratios agree in order of magnitude and in their order with those of Hess. The same values can hardly be expected, as impurities, water vapor, dust particles, for instance, of disintegrated metal have a large influence on the mobilities.

We proceed to calculate the mobilities of the ions. From the straight

lines we find for hydrogen the following values:

$$I = 2.10^{-4} \text{ amp.}; \qquad \text{I} = 24 \text{ cm.}; \qquad \Delta p_{H_2} = 0.45 \text{ cm. } H_2O$$

$$U_{H_2} = \frac{2.10^{-4}\, 3.10^9}{4\pi \cdot 24 \cdots 45 \cdot 981 \cdot 300} = 1.51\ 10^{-2}\ \frac{\text{cm.}}{\text{sec.}} : \frac{\text{volt}}{\text{cm.}}.$$

The results are collected in the following table.

Mobilities $\frac{\text{cm.}}{\text{sec.}} : \frac{\text{volt}}{\text{cm.}}$

	Corona.	α articles, Hess.	Point Discharge, Chattock.
U_{H_2}	$1.51 \cdot 10^{-2}$	$3.73 \cdot 10^{-2}$	5.4
U_{N_2}	$.505 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	
U_{CO_2}	$.161 \cdot 10^{-2}$	$.45 \cdot 10^{-2}$	.83
U_{O_2}	$.23 \cdot 10^{-2}$	$1.98 \cdot 10^{-2}$	1.3
U_{NH_3}	$.311 \cdot 10^{-2}$		

In most cases the mobilities are only about two times smaller than those determined by Hess; the mobility of oxygen however is 8.6 times smaller than the value obtained by Hess; this may be due to the formation of ozone which accompanies the corona discharge in oxygen. Conspicuous in the corona discharge as well as in the ionization by α particles are the small values of the mobilities compared with those of the point discharge for instance. We may expect other analogies in those forms of discharge which are distinguished by small mobilities of the ions.

We proceed to calculate the fraction of the heavy ions of Langevin. We write the formula (11) in the form:

$$\Delta p = \frac{en}{u}\,\frac{\text{I}}{4\pi},$$

or for one type of ions:

$$\Delta p_s = \frac{e}{4\pi}\,\frac{n_s}{u_s},$$

$$\Delta P = \Sigma \Delta p_s = \frac{e}{4\pi} \sum_{s=1}^{v} \frac{n_s}{u_s},$$

when there are v types of ions present. If $v = 2$, then

$$\Delta P = \frac{e}{4\pi}\left(\frac{n_1}{u_1} + \frac{n_2}{u_2}\right) \text{ and } i = e(n_1 + n_2).$$

The fraction of heavy ions is then put equal to α so that

$$n_2 = \alpha n,$$
$$n_1 = (1 - \alpha)n$$

and

$$\Delta P = \frac{en}{4\pi}\left(\frac{1-\alpha}{u_1}+\frac{\alpha}{u_2}\right) = \frac{i}{4\pi}\left[\alpha\left(\frac{u_1-u_2}{u_1u_2}\right)+\frac{1}{u_1}\right],$$

$$\alpha = \frac{1}{u_1-u_2}\left[\frac{\Delta P 4\pi}{i}u_1u_2 - u_2\right]$$

or in per cent.

$$\alpha = \frac{100u_2}{u_1-u_2}\left(\frac{\Delta P 4\pi u_1}{i}-1\right).$$

For air we have according to Pollock [1]

$$u_1 = 1.3 \text{ (volt)}; \qquad u_2 = .0003 \text{ (volt)}.$$

For electrostatic units of the field we multiply these numbers by 300;

$$i = \frac{I}{l} = \frac{2.10^{-4}\cdot 3.10^{9}}{24},$$

$$\Delta P = 3.981 \frac{\text{dynes}}{\text{cm.}^2} \text{ for oxygen.}$$

With these numbers we obtain $\alpha = 13.4$ per cent.

We shall now approximately determine the time which the pressure increase requires for its development. Let the average velocity of the ions be $v = uE$, then the average time required by the ions to pass through the distance $R_2 - R_1$ will be equal to

$$t = \frac{R_2 - R_1}{\bar{v}} \text{ and } \bar{E} = \frac{V}{R_2 - R_1},$$

where V is the potential difference between the cylinder and the wire.

$$t = \frac{(R_2 - R_1)^2}{u.V} = \frac{R_2^2}{u.V}.$$

For $R_2 = 2.25$ cm., $u = 5.05\cdot 10^{-3}$ (volt), $V = 15{,}000$ volts, we obtain $t = .067$ sec. If however we take into account the heavy ions, for which $u = 3\cdot 10^{-4}$, then we find $t = 1.1$ seconds, while C. S. Fazel found about 1.5 seconds. For the high mobilities $u = 1.3$ (volt) we find for $t = 2.6\cdot 10^{-4}$ seconds. For the explanation of the large pressure increase we have to assume the formation of heavy ions with very small mobilities. Apparently we can test this conclusion by means of alternating currents. Before doing this, we shall call attention to one or two corrections which have to be made in formula 10. If the ions which arise from the positive wire do not impart their momentum to the gas, they will impart it to the cathode and the gas pressure will not change.

The momentum imparted to the surface $2\pi R_2$ of the cylinder per unit time will be equal to

$$u_{R_2} E_{R_2} mn = (uE)_{R_2} \frac{m}{e} ne = (uE)_{R_2} \frac{m}{e} i = \Delta p_i 2\pi R_2.$$

In general only a fraction of the ions will transmit their momentum directly to the electrode, *i.e.*, to the outer cylinder, so that the pressure increase observed corresponds only to a certain fraction of the current; in formula (10) we have to diminish the current or to add to the pressure Δp a small positive correction Δp_i. We would have: $i/4\pi u = \Delta p + \Delta p_i$. In the manometer we observe only Δp. If the current $i = 0$, then $\Delta p = -\Delta p_i$; this seems to occur in the case of hydrogen according to Fig. 45 on page 85 of the bulletin. If on the other hand the gas molecules are reflected from the cylinder, then the gas pressure on an external surface element will be increased and we shall have a correction Δp_r in the form:

$$\frac{i}{4\pi u} = \Delta p - \Delta p_r.$$

If now $i = 0$, then $\Delta p = \Delta p_r$; a trace of this may occur in the straight lines of NH_3, O_2 and CO_2 in Fig. 45, where the straight lines meet the axis of ordinates a little above the origin. This effect of course could not be a stationary one.

From the explanation of the principal phenomenon it follows, that if we push the glass tube of the manometer from the cylinder more and more toward the wire, the pressure difference $p_2 - p_0$ can not change, provided that in that point the discharge does not change. If with this method nevertheless very small pressure differences have been observed for the two limiting positions of the gas tube, they can only be reduced to small secondary changes in the discharge. There exists indeed a pressure difference $p_1 - p_2$ which we have calculated, but it cannot be measured with the manometric method here indicated.

The straight lines which express the relation between the current and the pressure increase $p_2 - p_0$, have only been obtained for the positive corona, in which the wire is positive. If the wire is charged negatively, we observe also a pressure increase, which however is subject to strong fluctuations, so that regular observations cannot be repeated. This is apparently due to the character of the negative discharge, which does not spread out evenly over the wire, but consists of beautiful little beads, which are partly stationary, partly travel along the wire. For very short time intervals, however, immediately after the potential difference has been applied, the negative corona appears in the form of a fine uni-

form cylinder of light, which covers the whole wire. During this interval the negative corona pressure is probably stable.

If now we produce the corona with alternating current of frequency n, then during every positive and negative half wave the light ions will travel through the whole layer of gas from the wire to the cylinder, producing a partial pressure increase with a frequency $2n$. This phenomenon has been observed by C. S. Fazel.

If the wire is positive, large positive ions of small mobility will be formed, to which corresponds a large pressure increase dp according to the equation $i/u\, dr = dp 2\pi r$. These ions, however, will not reach the cylinder during the first positive half wave of the A.C. The corresponding pressure increase will not reach the manometer; if now the negative wave of the A.C. acts, the large ions may be neutralized or even become negative, they will stand still or travel a little further; if afterwards the wire becomes positive again, the quick positive ions will also charge positively those previously formed large ions, which will travel a little further toward the cylinder, which they will reach only after a certain number of cycles. Thus the resultant pressure increase will be equal to that of a corresponding direct current; upon this positive pressure increase are superimposed small regular fluctuations with frequency $2n$. This phenomenon also has been observed by C. S. Fazel.

It has been shown that the characteristic pressure increase in the corona discharge is due to the fact that the ions impart their momentum to the gas. The pressure increase is exactly proportional to the current. The mobilities are of the same order of magnitude as those determined by Hess. If we assume only ordinary ions and heavy Langevin ions, we find that the latter amount to about 13 per cent. of the total ionization. Of course it is possible that ions of widely different mobilities are formed as those studied by O. Blackwood [1] and P. J. Nolan.[2] The mobilities of the ions formed in the corona discharge will be measured by an independent method. The average time required for the formation of the pressure increase has been calculated. The pressure increase observed by C. S. Fazel with alternating currents has been explained.

I am glad to thank Dr. K. F. Herzfeld of the Institute for Theoretical Physics of the University of Munich for many valuable suggestions.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
October, 1921.

[1] PHYSICAL REVIEW, Vol. XVI., p. 85, 1920.
[2] PHYSICAL REVIEW, Vol. XVIII., p. 185, 1921.

BEHAVIOR OF FREE ELECTRONS TOWARD GAS MOLECULES.

BY H. B. WAHLIN.

SYNOPSIS.

Formation of Negative Ions in Gases.—The theories advanced to account for the appearance of abnormal negative mobilities at low pressures are two: it is assumed that in order to form an ion an electron must either have more than a certain amount of energy (Wellisch) or must have made, on the average, n impacts (J. J. Thomson). To test the Wellisch theory, *the effects of increasing the energy of the electrons* was determined. The fact that the number of ions was not increased is taken to favor the Thomson theory. Assuming this theory correct the *Thomson constant n was determined for* CO, NH_3, C_2H_4, C_2H_2, C_2H_6, C_2H_5Cl *and* Cl_2, using carefully purified gases under varying conditions of pressure and frequency of alternating potential. The results depend on the values assumed for the mobility of the electron in the various gases, but they indicate that for gases in the order given, n decreases progressively from about 10^8 for CO to 10^3 or less for Cl_2.

Conclusions.—CO behaves like N_2; electronegative gases attach electrons more readily than do electropositive gases; the degree of saturation of hydrocarbons does not make much difference.

Mobility of negative ions in chlorine, ethane and ethylene was found by the Rutherford A.C. method to be, respectively, 0.73, 1.30 and 0.91 cm./sec./volt/cm. at atmospheric pressure.

INTRODUCTION.

IN order to account for the fact that the mobility of the negative ion in a gas ceases to be inversely proportional to the pressure as the pressure decreases, Sir J. J. Thomson[1] developed a theory in which he assumes that the electron has to make, on the average, a number of impacts, n, with the molecules of a gas before uniting to form an ion. If this is the case, it is clear that an electron under the action of an applied electric field will travel a greater and greater distance in the direction of the field as the pressure decreases, before combining with the molecules of the gas. Then, since the velocity of drift of the electron in unit field is great compared with that of the ion, we would expect that the mobility as measured by any of the standard methods would be abnormally high. On his assumption, Thomson has shown that out of q_0 electrons starting from a given plane in a gas the number q that travel a distance x without uniting with the molecules of the gas is given by

$$q = q_0 e^{\frac{-wx}{nk'\lambda \frac{v}{d}}}, \qquad (1)$$

[1] Thomson, J. J., Phil. Mag. Sept., 1915.

where w is the mean velocity of agitation of the electrons, k' their mobility, λ the mean free path and v/d the applied potential gradient. In this form the equation is applicable to the Langevin method of measuring mobilities.

Loeb [1] modified this expression so as to make it applicable to the Rutherford method of determining mobilities, when a square wave alternating potential is used, and obtained as an expression for the current, I, to the electrometer

$$I = I_0 e \frac{-w}{nk'\lambda}\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right], \qquad (2)$$

where I_0 is the value of the saturation current corresponding to a voltage V, K' and λ are the mobility and the mean free path of the electron at a pressure of 760 mm., K the mobility of the ion at this pressure, p the pressure of the gas, d the distance between the plates and $1/N$ the time for a half cycle of the alternating potential. On the basis of this equation, Loeb determined the values of n for N_2, H_2, O_2, and air, assuming the mobility of the electron to be 200 cm./sec./volt/cm.

A further substitution may be made if the Townsend expression for the mobility of the electron, .

$$300K' = \frac{.815e\lambda}{mw},$$

is accepted as valid. Equation (2) then becomes

$$I = I_0 e \frac{-.815e}{300nm(K')^2}\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right]. \qquad (3)$$

This expression leaves K' as the only quantity about which there is any great degree of uncertainty. The value of K' for nitrogen has been determined by Loeb recently and has been found to be 2,800 cm./sec./-volt/cm., at a pressure of 75 mm. of mercury and in a field of 20 volts. Just what the values of K' will be in other gases, we cannot at present say, and until these values have been determined, we must make an assumption which probably only approximates the truth. This assumption is that the mobility of the free electron in a gas varies from gas to gas in the same manner as does the mobility of the negative ion. Equation (3) then becomes, when we substitute the known values for e and m,

$$I = I_0 e \frac{-1.9 \times 10^8}{n}(K_{n/K})^2\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right], \qquad (4)$$

where K_n is the mobility of the negative ion in nitrogen.

[1] Loeb, L. B., PHYS. REV., Feb., 1921.

From this equation n may be calculated from an experimental current-voltage curve. This is done by substituting the quantities for a point on the curve in equation (4). Owing to the assumptions made in deducing this equation, it is necessary to choose a point near the asymptotic foot of the curve. The value of n thus calculated is very nearly a constant, for varying frequencies of the alternating potential and varying pressures, and in the gases studied by Loeb appears to be characteristic of the gas used. The writer will, in the following pages, present evidence which will assist in showing in how far this is the case and to what extent some of the factors which might influence the attachment of electrons effect the value of n.

Factors Influencing the Attachment of Electrons.

There are three factors which might influence the attachment of electrons in gases:

First, an abnormal condition of the gas such as the presence of an activated form or a particular state of the molecules as regards the electronic arrangement in the outer structure. It is well known that when α-particles or ultra-violet light passes through some gases, changes take place. For example, in oxygen we have ozone (O_3) formed and it is possible that this might attach the electrons more readily than do the O_2 molecules. Now, in general, the amount of activation when ultra-violet light is used to produce the electrons would be comparatively small, but if an electron attaches at every impact with these activated molecules, the effect of a small amount of the impurity would be to change the result greatly. However, in some of the determinations made, the writer varied the intensity of the ultraviolet light by a factor of four with no noticeable change in the readiness with which the electrons attach. Where α-particles are used as a source of ionization, it is possible that enough complete chemical change would be produced to influence the value of n for a gas very markedly.

The second possibility is that the electrons must strike the molecules in a certain place in order to attach.

The third factor that might influence the attachments is the relative energy of the electron and molecule at impact. For in the light of our present knowledge of atomic structure, it is conceivable that the electron must have a certain critical energy of approach in order to combine with the molecule. The question which we must decide, then, is whether or not the mean energy of thermal agitation is sufficient to cause attachments and whether or not an increase of the energy of the electrons above that of agitation will influence the constant of attachment, n. This

question can be answered experimentally as the following considerations will show.

THE EFFECT OF ENERGY ON THE ATTACHMENT OF ELECTRONS.

Wellisch,[3] using the Franck modifications of the Rutherford method for measuring mobilities, found below a pressure of 8 cm. in air, evidence for two types of carriers of negative electricity. One type showed the normal variation of mobility with pressure. The other gave abnormally high mobilities with decreasing pressures. Carriers of this second type, Wellisch considered to be free electrons, and he accordingly concluded that the negative carriers in a gas consist of normal ions and permanently free electrons. To account for these free electrons, he assumed that the energy of the electron at impact must exceed a certain value in order to combine to form an ion. To account for the two kinds of carriers observed, the energy would have to exceed the mean energy of thermal agitation, and Wellisch assumed that this additional energy required comes from the energy of emission of the electrons. In short, the explanation he offered was that in order to make an attachment, the electron must strike another molecule within a certain distance of the parent molecule; *i.e.*, before its kinetic energy of emission has decreased below the critical value necessary to form an ion.

If this explanation is to hold, we should expect that in the Wellisch experiment, there would be no change in the nature of the mobility curves obtained with increasing values of the field driving the electrons through the gauze, until the velocity acquired in the field became comparable with the velocity of emission of the electrons from the molecules under the influence of α-rays. For a small change in the field would not materially alter the chance an electron has of striking a molecule within a certain distance of the molecule from which it comes, the velocity of emission being great compared with the velocity acquired in the field. That the curves actually do change their form for relatively small changes in the field was shown by Loeb,[2] who found that as the auxiliary field is increased, the evidence for the two types of carriers disappeared entirely. This indicates weakness in the Wellisch theory.

A further test of this theory may be made by increasing the energy of the electrons in the auxiliary field to a higher value than was used in the experiments by Loeb, for it is to be expected on the basis of the Wellisch theory that before the electron gains ionizing energy in the field, the number of free electrons passing through the gauze would fall to zero, because the energy acquired by the electrons between impacts would

[3] Wellisch, E. M., Am. Journal of Science, 4, 39, p. 583, 1915. Am. Journal of Science, 4, 44, p. 1, 1917.

then exceed the energy of emission from the molecules when the gas is ionized by α-particles. The electrons would therefore be making impacts with the molecules equal to or exceeding the energy necessary for attachment.

In order to determine whether this is the case, the writer converted the apparatus as used by Loeb in his determination of n, to one of the Wellisch type, the only difference being that whereas Wellisch used a radioactive substance to produce his ionization, the writer obtained his photoelectrically, by letting ultra-violet light strike a speculum metal plate. Fig. 1 (*a*) is a plate of speculum metal; (*b*) is a battery which

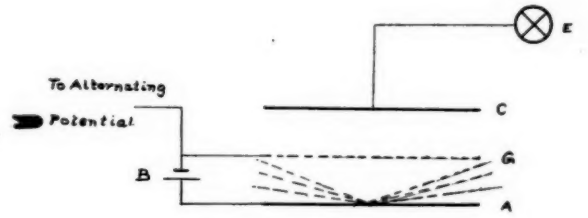

Fig. 1.

produces the field for driving the electrons and ions through the gauze (*g*). (*c*) is a collecting plate 10 cm. in diameter connected to the electrometer (*e*). The alternating potential is connected to the gauze. The distance from (*a*) to (*g*) was made 1.5 cm. and the distance from (*g*) to (*c*) 1.3 cm. The gauze was made by boring holes 1 mm. in diameter in a sheet of brass one half mm. in thickness, the distance between adjacent holes being about 1 mm. With this gauze the writer encountered no difficulty due to the stray field carrying a charge to the collecting plate. Tests were made for a stray field by varying the distance between the collecting plate and the gauze. The current corresponding to a given value of the alternating potential was measured by noting the charge acquired by the collecting plate in a given time. In all this work air was used at pressures of 8 cm. and below. With pressures of from 4 to 8 cm., and with values of the auxiliary field of from 3 to 15 volts/cm., the two types of carriers noted by Wellisch were observed.

As is shown in Curve I. (Fig. 2*A*), with an auxiliary field of 9 volts and at a pressure of 4 cm., the two types of carriers observed by Wellisch are present. With an auxiliary field of 150 volts (II., Fig. 2*A*), the evidence for the two kinds disappears entirely. If the carriers were the normal ions only, this curve as well as III. and IV. in Fig. 2*B*, which were obtained with auxiliary field of 640 and 1,400 volts respectively, should strike the voltage axis at about 35 volts. The curves do change

their form in that the current corresponding to a given voltage decreases for high values of the auxiliary fields. This, however, cannot be taken as evidence for an increase in the number of ionic carriers, as the saturation currents taken with a steady potential showed this same tendency.

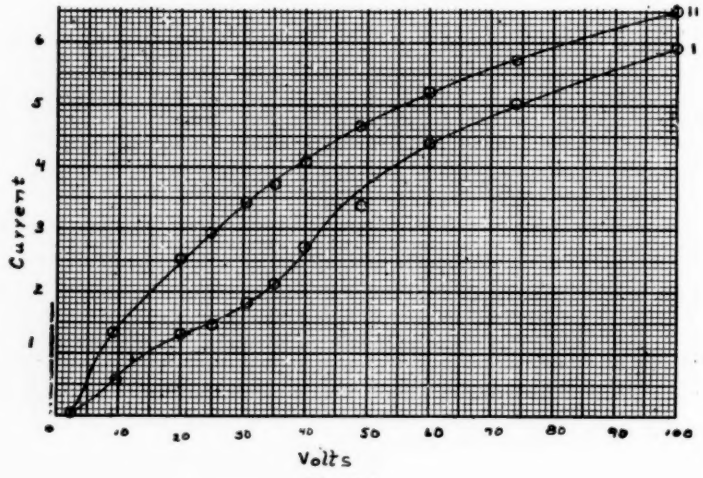

Fig. 2*A*.

Pressure 4 cm. Frequency of alternating potential, 710 alternations per sec. I.—auxiliary field—9 volts. II.—auxiliary field—150 volts.

We see from these results that an increase in the energy of the electrons above that of thermal agitation does not appreciably influence the number of attachments, and must conclude that the mean energy of agitation at ordinary temperatures is sufficient to cause the electrons to combine with the molecules. This makes the Wellisch theory untenable and leaves as the only alternative which we at present have, the Thomson theory.

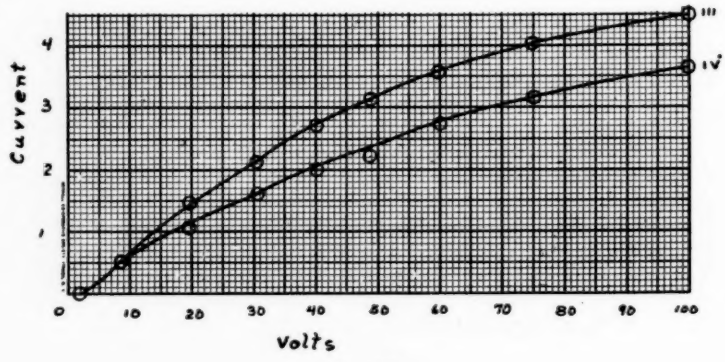

Fig. 2*B*.

Pressure 4 cm. Frequency of alternating potential 710 alternations per sec. III.—auxiliary field of 640 volts. IV.—auxiliary field of 1,400 volts.

It next becomes of interest to determine the constant, n, of the Thomson theory to see how it varies in different gases with the chemical nature of the gases and with the different types of chemical bonds between the atoms of the molecules of which the gas is composed. Results of this kind may furnish data that will help us to a better understanding of outer atomic and molecular structure.

DETERMINATION OF THE THOMSON CONSTANT.

In general, the method used in the determination and calculation of n was the same as that used by Loeb in his experiments. The writer has found the value of n for seven gases; viz., CO, NH_3, C_2H_2, C_2H_4, C_2H_6, Cl_2 and C_2H_5Cl. The determinations were made on at least five different samples of each of the gases, and a number of mobility curves under varying conditions of pressure and frequency of the alternating potential were obtained from each sample. In most cases the pressure variation ranged from 7.6 cm. to 76 cm. and the fréquency from 145 alternations/sec. to 712 alternations/sec. Whenever possible, the mobility of the negative sion was determined, and if this could not be done, the values found by other observers were used. In making a series of determinations, the chamber was washed out four or five times with the gas being used, by filling to atmospheric pressure, exhausting to a pressure of 1.5 cm., and filling again. Thus the residual gas from any previous determinations was very small. The value of n was calculated from ten to twelve of the most representative curves for each gas.

In the preparation of the gases, considerable care was taken to get them pure. The importance of this is shown in the work on hydrogen by Loeb. He obtained electronic mobilities in this gas at atmospheric pressure, where other observers had been able to get comparatively low mobilities only. Furthermore, the method of preparation chosen for each gas was such that any impurity present would cause only an unappreciable number of attachments, for obviously the presence of a small percentage of an impurity which attaches electrons readily would change the value of n far more than one which does not. The method of preparation and purification of each gas follows:

PREPARATION AND PURIFICATION OF GASES.

Carbon monoxide was prepared by the action of concentrated sulphuric acid on sodium formate. The gas evolved was bubbled through a solution of sodium hydroxide in a tower packed loosely with glass wool, which served to break up the bubbles and retard their progress through the solution. The gas was then passed over calcium chloride to remove

any excess of water vapor and over hot copper to break up any organic impurity and remove free oxygen. If there were a trace of oxygen present, there would be some carbon dioxide formed at this point, and in order to remove this, the gas was passed over solid sodium hydroxide. It was then passed over calcium chloride and phosphorous pentoxide to complete the drying, through two traps cooled to liquid air temperatures and finally into the chamber. The cooling served to remove the last trace of any of the more easily condensible impurities. Density tests on the gas checked with the true value to within one part in two thousand.

Ammonia was prepared by heating a solution of ammonium chloride and sodium hydroxide to boiling. A reflux condenser connected to the generating flask removed the excess of water vapor. From this the gas passed over calcium oxide to remove any water remaining and was next liquified in a trap cooled to $-112°$ with frozen alcohol. The liquid ammonia was boiled under reduced pressure to remove oxygen and any of the more volatile impurities, and the liquid thus purified was allowed to vaporize into the chamber first passing through a trap cooled to $-26°$ to remove vapors of stopcock greases.

Acetylene was prepared by the action of water on calcium carbide. The gas was first passed through a series of wash bottles containing solutions of cupric sulphate made slightly acid with sulphuric acid. This removed hydrogen sulphide and phosphine, which are the chief impurities present in acetylene prepared from the commercial carbide. The gas then passed over calcium chloride for a preliminary drying, through a trap cooled to $-26°$ with frozen carbon tetrachloride and was condensed in a second trap cooled with frozen alcohol. About one third of the condensed acetylene was evaporated under reduced pressure. The next third was passed over calcium chloride and phosphorous pentoxide, through a trap cooled to $-26°$, and into the chamber. The remaining third of the gas escaped to the air directly. By this method of fractionation, the less volatile as well as the more volatile impurities would be removed.

Ethylene was prepared by the common laboratory method; *i.e.*, by heating a mixture of concentrated sulphuric acid and ethyl alcohol to a temperature of 165°. The gas evolved was passed through water to remove any alcohol that would be carried over, and through solutions of sodium hydroxide to remove any sulphur dioxide and sulphur trioxide fumes. The water and sodium hydroxide solutions would also remove the greater part of the ether that is evolved in the process. Next the ethylene passed over calcium chloride, then through a trap cooled to $-85°$ with frozen methyl alcohol, and was condensed in a second trap

cooled to $-112°$ with frozen ethyl alcohol. The gas was fractionated and dried by the same method used for acetylene, and then passed through a trap cooled to $-85°$ into the chamber.

Ethane[1] was prepared by the electrolysis of a concentrated solution of sodium acetate in water, the solution being made slightly acid with acetic acid. In the process, hydrogen is given off at the cathode and a mixture of ethane and carbon dioxide at the anode. Care was taken to keep the solution cool during the electrolysis as the efficiency of the process decreases very much with an increase in temperature. Some acetic aldehyde is formed due to the reducing action of the hydrogen, but this, together with the carbon dioxide liberated, was removed by passing the gas through a number of solutions of sodium hydroxide. The process of drying and fractionating was the same as that used for acetylene. Before entering the chamber the gas passed through a trap cooled to $-28°$.

Ethyl chloride was obtained in a pure state from the tubes used by the medical profession for freezing purposes, but was passed through a dilute solution of sodium hydroxide to remove hydrochloric acid gas and then through a solution of sodium thiosulphate to remove any free chlorine that might be present. It was then condensed in a trap cooled to 0°. The process of fractionation and drying was the same as that used for acetylene.

Chlorine was obtained from a tank kindly furnished by Dr. G. L. Wendt, of the Department of Chemistry. During the first two fillings the gas was condensed and fractionated and then dried by passing it over phosphorus pentoxide before it entered the chamber. It was found advisable, however, to dispense with the fractionation, since the gas reacted so rapidly with the metallic surfaces of the chamber that it was necessary to make a filling and take the data in as short a time as possible.

DETERMINATION OF n FOR AIR AND CHLORINE.

The writer was unable to get any appreciable photoelectric emission in the presence of chlorine. Although a number of metallic surfaces of different materials were tried, in no case was the emission great enough to be of any use in this experiment. The apparatus was, therefore, converted into one of the Wellisch type, and the ionization was produced by α-particles from polonium. The polonium was deposited on a copper plate which was fastened to the lower side of the gauze (g),

[1] This method is preferable for this experiment to the accepted one for preparing pure ethane; viz., by the action of a zinc-coppered couple on an alcoholic solution of ethyl iodide, since the presence of a trace of any of the halogens as an impurity would alter the results enormously.

(Fig. 1). Care was taken so as to shield the upper part of the chamber from the radiation.

In order that this method shall be applicable to the Thomson theory, the calculations must be made from curves obtained at pressures so low that at least a portion of the electrons liberated pass through the gauze before combining with the molecules of the gas. In other words, the curves must be such as to show the two types of carriers noted by Wellisch. To determine to what extent the method is applicable to the Thomson theory, a series of determinations of n for air was first made. Fig. 3

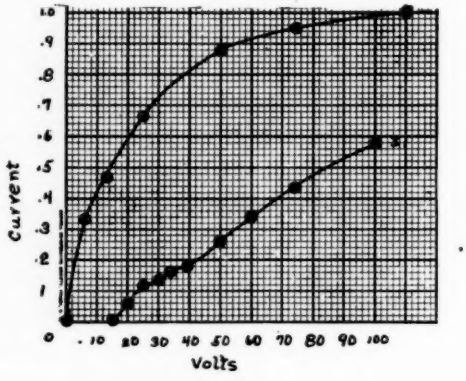

Fig. 3.

Pressure 7.5 cm. Frequency of alternating potential 712 alternations per sec. Auxiliary field—6.0 volts. I.—Mobility curve. II.—Saturation curve. The current is given in fractional parts of the saturation current at 100 volts.

illustrates the type of curve obtained at a pressure of 7.5 cm. The lower part of this curve; *i.e.*, below 42 volts, is due to electrons which get through the gauze before combining. These then start from the gauze as do the photoelectrons in the other determinations of n, and it is therefore from this portion of the curve that our calculations must be made. In this case, the value of I_0 cannot be taken as the value of the saturation current corresponding to the voltage in question. For, obviously, the saturation current is made up of two parts—one part of the current being due to the carriers which start from the gauze as ions and the other part being due to those carriers which start from the gauze as electrons. It is this latter part which determines the value of I_0 in equation 4. Since there is no way in which a distinction between the two types can be made in the case of the saturation current, an approximation to the true value was obtained by assuming I_0 to be equal to the value of the mobility current at the voltage in each case where the electronic carriers predominate. In Fig. 3 this would correspond to the value at 42 volts. However, since the calculations must be made from the lower parts of

the mobility curves, it is necessary to correct this value further for the change in the saturation current as the voltage decreases. So that the value of I_0 thus obtained must be multiplied by the ratio of the saturation current at the voltage in question to the value of the saturation current at the voltage at which I_0 is chosen. In general, a determination thus made would give too low a value for the saturation current, but since in the determination of n, only the logarithm of I/I_0 enters, the error would not be enough to change the results by an appreciable factor. The value of n thus calculated was found to be 4.1×10^4 which compares very favorably with the value of 4.3×10^4 as found by Loeb.

No abnormal mobilities could be obtained in chlorine even at pressures of 1.3 cm. The writer could not work at pressures below this for the ionization produced by the α-particles became so small that the currents were difficult to measure. However, an upper limiting value of n may be calculated if it is assumed that the least ration of I/I_0 that could be measured is .03. Then for the voltage just below the value at which the mobility curve strikes the voltage axis, and for values of the pressure, frequency, and plate distance corresponding to the conditions under which the curve was obtained, a value of n was determined. This will be given in the table below.

Table of Results.

Gas.	n from Equation (4).	K Ionic Mobility.	n from Equation (2).	Limits of Variation of n in Equation (2).	Observer.
N_2.....	Infinite	2.50	Infinite	——	Loeb
H_2.....	Infinite	——	Infinite	——	Loeb
CO.....	1.6×10^8	1.20	3.1×10^7	$(1–6) \times 10^7$	Wahlin
NH_3.....	9.9×10^7	0.78	1.3×10^7	$(.7–1.6) \times 10^7$	Wahlin
C_2H_4.....	4.7×10^7	0.91	7.1×10^6	$(.18–1.6) \times 10^7$	Wahlin
C_2H_2.....	7.8×10^6	1.15	1.5×10^6	$(0.8–2.3) \times 10^6$	Wahlin
C_2H_6.....	2.5×10^6	1.30	5.3×10^5	$(2.5–8.8) \times 10^5$	Wahlin
CO_2[1].....	1.5×10^7	1.22	2.9×10^6	$(2.3–4.3) \times 10^6$	Loeb
CO_2[2].....	3.5×10^6	1.22	6.9×10^5	——	Loeb
CO_2[3].....	2.1×10^5	1.22	4.0×10^4	——	Loeb
N_2O[4].....	6.1×10^5	1.33	1.4×10^5	$(0.8–2.3) \times 10^5$	Loeb
N_2O[5].....	3.6×10^5	1.33	7.8×10^4	——	Loeb
C_2H_5Cl.....	3.7×10^5	0.30	1.8×10^4	$(1.3–2.8) \times 10^4$	Wahlin
Air[6].....	4.1×10^4	2.50	1.7×10^4	$(0.7–5.7) \times 10^4$	Wahlin
Air.....	4.3×10^4	2.50	1.8×10^4	$(0.7–6.4) \times 10^4$	Loeb
O_2.....	8.7×10^3	2.50	3.6×10^3	$(1.5–5.7) \times 10^3$	Loeb
Cl_2.....	Less than 2.1×10^3	0.73	Less than 240	——	Wahlin

[1] Freshly prepared.
[2] 4 hours old.
[3] 22 hours old.
[4] Freshly prepared.
[5] 24 hours old.
[6] Using γ-particles.

RESULTS OF DETERMINATION OF n.

The table above gives the values for the mobility of the negative ion used in the calculations of n. It also gives the value of n as calculated from equation 2 and from equation 4, assuming electronic mobility to be proportional to the mobility of the negative ion in both cases.

The values given for the mobility of the negative ion are in most cases higher than the generally accepted values, but the Rutherford method of measuring mobilities gives results which in general are higher than those obtained by other methods. As far as the writer has been able to learn, this is the first time the mobility of the negative ion in ethane, ethylene and chlorine have been determined. Rutherford, however, measured the sum of the mobilities of the positive and negative ions in chlorine and found for this value 2 cm. per sec. per volt per cm. The results on ethane and ethylene were obtained using the Rutherford method and those on chlorine by using the Franck modification of this method.

DISCUSSION OF RESULTS.

As will be seen from these results, the values for n calculated on the basis of equation (4) do not agree with those from equation (2), assuming in each case the mobility of the electron to be proportional to that of the ion and independent of the pressure and field strength. Unfortunately our data on electronic mobility are as yet too meager to tell us which set of values most nearly approximates the truth, but whichever set is chosen, the values will serve for comparison of the relative electronic affinites for different gases.

In most cases the value of n is high, showing that the electron does not readily attach itself to a molecule. The fact that in no case is the variation for any gas outside the limits of experimental error indicates that the value of n for a gas is characteristic of that gas. This is further indicated by the fact that the value found for air, using the Franck modification of the Rutherford method and using α-particles as the ionizing source, checks with Loeb's result which he obtained producing the electrons photoelectrically.

It is highly probable that the electron must have a certain critical energy of approach in order to combine to form an ion, but as has been shown, this critical energy is less than the mean energy of thermal agitation, since an increase of the energy of the electrons above that of agitation does not measurably influence the attachments. This leaves two alternatives in explanation of these results; viz., either the electron must strike the molecule in some particular place, or the electron must strike the molecule in some particular state. Whichever explanation holds,

the Thomson theory is still valid, so we have no means of differentiating between the two from the results above.

The fact that n for air is about 5 times the value for O_2 indicates that it is to the O_2 molecule in air that the electron attaches. This would also be indicated by the fact that the N_2 and H_2 molecules do not attach electrons. It is not surprising that these gases give no attachments, for the reluctance the molecules of these gases show for acquiring a negative charge has already been observed by methods of positive ray analysis. J. J. Thomson in his "Positive Rays" states that in no case has a negatively charged nitrogen molecule ever been observed, and only rarely a negatively charged hydrogen molecule.

On account of the resemblance between nitrogen and carbon monoxide as regards a number of their chemical and physical properties, Langmuir[1] and more recently, Thomson[2] have assigned to the molecules of the two gases the same outer molecular structure. Thomson further points out that we should therefore expect a similarity in behavior between the two as regards electronic attachments. As may be seen from the value of n for CO, only rarely does an electron attach to form an ion. In fact, it is possible that it never does. The writer was able to get mobilities for the negative ion in CO of 240 cm./sec. per volt per cm., and although on the Thomson theory this has no significance as a mobility measurement, it will serve to show that the electron will remain free in the gas an appreciable length of time. Such high mobilities have never been obtained before. In the case of NH_3 it is to be expected that the electron will not attach readily, for the NH_3 molecule tends to attach a positively charged hydrogen ion whenever possible and should therefore not show a high degree of electronic affinity.

The results on acetylene, ethylene, and ethane show that as far as the attachments are concerned, there is very little difference between molecules having a double, triple, or a single bond. In a recent paper on the structure of molecules and chemical combinations, J. J. Thomson states that the attachment of an electron to a molecule having a single bond between the atoms might sufficiently loosen the contacts between the atoms so that the molecules would break up. Unfortunately a determination of the mobility of the ion in a gas furnishes us no means for determining if this is the case, since, as has been shown by Wellisch[3] and Franck,[4] the mobility of carriers of atomic dimensions is independent of the size of the carrier. Although it is possible that in some cases the

[1] Langmuir, Irving, Jour. Am. Chem. Soc., 41, 6, p. 868, 1919.

[2] Thomson, J. J., Phil. Mag., March, 1921.

[3] Wellisch, E. M., Proc. Roy. Soc., 82A, 509, 1909.

[4] Franck, 9 Ber. d. Dtsch. Phys. Ges., 11, 397, 1909.

attachment of an electron will cause the molecule to split up into a negatively charged atom and a neutral one, it does not seem possible that in a comparatively inert gas like ethane, in which the bond between the two carbon atoms remains intact in most chemical reactions if not in all, the energy of the electron at impact would be sufficient to cause the molecule to break up into a negatively charged atom and a neutral CH_3 group.

The aging effect observed by Loeb in carbon dioxide is as yet unexplained. He prepared the gas by treating pure marble with hydrochloric acid. The writer made a number of determinations in which the gas was prepared by heating sodium bicarbonate, but was unable to get any aging effect. The value of n in this case was more nearly equal to the lowest value in the table above; *i.e.*, to the value after aging. However, the gas in this instance was purified by fractionation and it is possible that in the process of condensation and evaporation, the effect is lost. Loeb also noticed a slight change in N_2O with time and explained it as being due to a dissociation of the gas into N_2 and O_2.

The comparatively high degree of electronic affinity of O_2 and Cl_2 is not surprising, since it is to be expected that the electronegative elements; *i.e.*, those which tend to gain electrons, should show a greater number of attachments than do the electro-positive elements. Furthermore, chlorine, being the more electro-negative of the two, shows the greater tendency to form a negative ion.

That the degree of electronic affinity is determined by the atoms of the molecule rather than by the bonds between the atoms is indicated by the results on ethyl chloride. For by a comparison of the results on this gas with the results on ethane, we see that the replacement of one of the hydrogen atoms with one of chlorine increases the number of attachments appreciably.

This problem was assigned by Dr. R. A. Millikan and was carried out under the directions of Dr. L. B. Loeb. The author wishes to express his thanks to these gentlemen for suggestions and criticisms throughout the progress of the work.

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NOTE ON THE GRAVITATIONAL ACCELERATION OF BISMUTH.

By Harold H. Potter.

Synopsis.

Gravitational acceleration of bismuth has been determined by the pendulum method and found to be the same as that for brass to at least one part in 50,000. This result contradicts the claim recently made by Brush that the acceleration for Bi is much less than for Zn.

In a recent number of the Physical Review,[1] C. F. Brush claimed to have proved by various methods that the gravitational constant for bismuth was less than that for zinc in the ratio 72 to 100. A simple pendulum of suitable design being already in use in this laboratory, Brush's results were checked by the pendulum method.

The pendulum used consisted of a hollow brass bob accurately cylindrical inside and out, suspended by a steel wire from an agate knife edge. The substance on which the experiment was being made was turned into a cylindrical form and fixed inside the hollow brass bob. The method of procedure closely resembled that adopted by Bessel[2] in his famous pendulum experiments. The period of the "experimental" pendulum was compared with that of a standard invar pendulum. A long series of experiments carried out in collaboration with Prof. O. W. Richardson showed that the period of the experimental pendulum—after all necessary corrections had been applied—did not vary by more than one part in 250,000 when various metals were placed in the hollow brass bob.

On the appearance of Brush's paper a cylinder of bismuth was carefully lathe-turned and placed in the bob of the experimental pendulum. The period of the pendulum was then measured, and after the usual corrections had been applied it was found that the period of the pendulum containing bismuth did not differ from that containing brass by more than one part in 250,000. Thus to the limit of accuracy of the experiment the gravitational acceleration for bismuth is the same as that for brass.

An accuracy of one in 250,000 in period represents an accuracy of

[1] C. F. Brush, Phys. Rev., Aug., 1921, p. 125.

[2] F. W. Bessel, Memoire relatifs à la Physique, V., p. 71.

one in 125,000 in the gravitational acceleration. The bismuth weighed 80 gms. out of a total for the whole pendulum of 220 gms.; hence the experiments described above show that the gravitational acceleration for bismuth is the same as that for brass to at least one part in 50,000.

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